

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-280202

(43)Date of publication of application : 02.10.2003

(51)Int.Cl.

G03F 7/039

H01L 21/027

(21)Application number : 2002-084074

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(22)Date of filing : 25.03.2002

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(54) POSITIVE RESIST COMPOSITION**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a positive resist composition suitable for use under an exposure light source of ≤ 160 nm, particularly F2 excimer laser light (157 nm) and to concretely provide a positive resist composition ensuring small line edge roughness and few development defects.

SOLUTION: The positive resist composition comprises (a) a resin in which a group which is released by decomposition by the action of an acid contains at least one fluorine atom and a cyclic structure and which is decomposed by the action of an acid to increase solubility in an aqueous alkali solution, (b) a compound which generates an acid upon irradiation with an actinic ray or a radiation and (c) a solvent.

LEGAL STATUS

[Date of request for examination] 27.05.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's

decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] (a) The compound which generates an acid by the exposure of the resin whose solubility over an alkali water solution the radical from which it secedes by decomposition by operation of an acid decomposes according to the operation of an acid containing at least one fluorine atom and cyclic structure, and improves, (b) activity beam of light, or a radiation, and the positive-resist constituent characterized by containing the (c) solvent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive-resist constituent used suitable for micro lithography processes, such as manufacture of a VLSI and a high capacity microchip, and other photofabrication processes. Furthermore, it is related with the positive-resist constituent which can form in detail the pattern made highly minute using vacuum ***** 160nm or less.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a quarter micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. As one of the means which attains detailed-ization of a pattern, short wavelength-ization of the exposure light source used in the case of the pattern formation of a resist is known.

[0003] For example, i line (365nm) of a high-pressure mercury-vapor lamp has been used for manufacture of the semiconductor device of the degree of integration to 64M bit as the light source to current. As a positive resist corresponding to this light source, many constituents containing the naphthoquinonediazide compound as novolak resin and a sensitization object were developed, and sufficient result has been stored in processing of the line breadth to about 0.3 micrometers. Moreover, instead of i line, KrF excimer laser light (248nm) has been adopted as manufacture of the semiconductor device of a 256 M bit or more degree of

integration as the exposure light source. Furthermore, in order to form the activity of the ArF excimer laser light (193nm) which is the light source of short wavelength, and a pattern 0.1 more micrometers or less from recent years for the purpose of semi-conductor manufacture of the degree of integration beyond 1G bit, the activity of F2 excimer-laser light (157nm) is considered.

[0004] According to short-wavelength-izing of these light sources, the constituent and its compound structure of a resist ingredient are also changing a lot. The constituent which combined the compound (photo-oxide generating agent) which generates an acid in the exposure of far-ultraviolet light, and the so-called chemistry magnification mold resist have been developed using the resin which made the basic frame small Pori (hydroxystyrene) of absorption in 248nm field as a resist constituent for exposure by KrF excimer laser light, and was protected by the acidolysis radical as a principal component.

[0005] Moreover, the chemistry magnification mold resist which used the acidolysis nature resin which introduced into the principal chain or side chain of a polymer the alicyclic structure which does not have absorption in 193nm as a resist constituent for ArF excimer laser light (193nm) exposure has been developed.

[0006] As opposed to F2 excimer-laser light (157nm) Also in the above-mentioned alicycle mold resin, it becomes clear that absorption of 157nm field is large and inadequate for obtaining the pattern 0.1 micrometers or less made into the object. On the other hand, it is reported by Proc.SPIE.Vol.3678.13 page (1999) that the resin which introduced the fluorine atom (perfluoro structure) has sufficient transparency for 157nm. the structure of an effective fluororesin -- Proc.SPIE.Vol.3999.330 page (2000) -- said -- 357 pages (2000) -- said -- it is proposed by 365 pages (2000), WO -00/No. 17712, etc., and examination of the RESHISUTO constituent containing fluorine content resin has been made.

[0007] However, the resist constituent containing the fluororesin for F2 excimer-laser light exposure has problems, like there are many line edge roughness and development defects, and solution of these points was desired. Line edge roughness means originating in the property of a resist and presenting the configuration where the line pattern of a resist and the edge of a substrate interface were irregularly changed in the direction vertical to the direction of a line. When this pattern is observed from right above, an edge is visible to unevenness (**several nm - about dozens of nm). When this unevenness has large unevenness, it causes a poor electrical property and makes the yield fall, since a substrate imprints according to an etching process.

[0008]

[Problem(s) to be Solved by the Invention] Therefore, the object of this invention is offering 160nm or less and the especially suitable positive-resist constituent for the activity of the exposure light source of F2 excimer-laser light (157nm), and is specifically offering a positive-resist constituent with small line edge roughness and number of development defects.

[0009]

[Means for Solving the Problem] this invention person etc. reached [that the object of this invention is attained with the following specific constituents, and] a header and this invention, as a result of inquiring wholeheartedly with careful attention to many above-mentioned properties. That is, this invention is the following configuration.

[0010] (1) The compound which generates an acid by the exposure of the resin whose solubility over an

alkali water solution the radical from which it secedes by decomposition by operation of the (a) acid decomposes according to the operation of an acid containing at least one fluorine atom and cyclic structure, and improves, (b) activity beam of light, or a radiation, positive-resist constituent characterized by containing the (c) solvent.

[0011] Hereafter, following the (2) – (7) is further mentioned as a mode of desirable operation of this invention.

(2) A positive-resist constituent given in the above (1) characterized by containing the structure by which the above-mentioned resin (a) is shown by the general formula (X1).

[0012]

[Formula 1]

[0013] among a formula, even if R1 and R2 are the same, they may differ from each other, and they express a hydrogen atom or an alkyl group. L expresses single bond or a divalent connection radical. X expresses the radical which has at least one of a fluorine atom and the fluoro alkyl groups, and at least one of alicycle structure and the ring structures.

[0014] (3) A positive-resist constituent given in the above (1) characterized by containing the structure by which the above-mentioned resin (a) is shown by the general formula (X2).

[0015]

[Formula 2]

[0016] (R1, R2, L, and X are similarly defined in the above-mentioned formula (X1) among a formula.) L' expresses an alkylene group, a cyclo alkylene group, an arylene radical, or an aralkylene group.

[0017] (4) The above (2) characterized by choosing Above X from the following, or a positive-resist constituent given in (3).

[0018]

[Formula 3]

[0019] (AC expresses alicycle structure among a formula.) n expresses the integer of 1–3. L expresses single bond or a divalent connection radical.

[0020] (5) A positive-resist constituent given in the above (4) characterized by choosing Above X from the following.

[0021]

[Formula 4]

[0022] (M expresses single bond or a double bond among a formula.) even if G1 and G2 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, a fluoro alkyl group, a cyano group, or a hydroxyl group. n expresses 0 or 1.

[0023] (6) A positive-resist constituent given in the above (1) whose above-mentioned resin (a) is characterized by having one repeat unit of the following general formulas.

[0024]

[Formula 5]

[0025] (A expresses among a formula the radical chosen from a hydrogen atom, a methyl group, a cyano group, a trifluoromethyl radical, a fluorine atom, a chlorine atom, and a bromine atom.) even if R1 and R2 are the same, they may differ from each other, and they express a hydrogen atom or an alkyl group. L expresses single bond or a divalent connection radical. L' expresses an alkylene group, a cyclo alkylene group, an arylene radical, or an aralkylene group. X -- a fluorine atom and a fluoro alkyl group -- the radical of either, alicycle structure, and ring structure which has either at least is expressed at least. n expresses 0 or 1.

[0026] (7) A positive-resist constituent given in either of above-mentioned (1) - (6) to which the above-mentioned resin (a) is characterized by having the following repeat unit (Z1) - (Z3) either further.

[0027]

[Formula 6]

[0028] (A expresses among a formula the radical chosen from a hydrogen atom, a methyl group, a fluorine atom, a chlorine atom, a bromine atom, a trifluoromethyl radical, and a cyano group.) Q expresses a hydrogen atom, an alkyl group, an aralkyl radical, or an aryl group. However, although Q may be acidolysis nature, both a fluorine atom and cyclic structure are not simultaneously included in Q in that case. n expresses 0 or 1.

[0029]

[Embodiment of the Invention] Hereafter, the compound used for this invention is explained to a detail.

[1] Resin (a component)

In this invention, resin (a) is resin whose solubility over an alkali water solution the radical from which it secedes by decomposition by operation of an acid decomposes according to the operation of an acid containing at least one fluorine atom and cyclic structure, and improves. Cyclic structure may have the bridging. as the radical which has the radical from which it secedes according to an operation of an acid -- for example (X1) -- and (X2) it is mentioned.

[0030]

[Formula 7]

[0031] among a formula, even if R1 and R2 are the same, they may differ from each other, and they express a hydrogen atom or an alkyl group. L expresses single bond or a divalent connection radical. X -- a fluorine atom and a fluoro alkyl group (alkyl group which has at least one fluorine atom) -- the radical of either, alicycle structure, and ring structure which has either at least is expressed at least.

In addition, the radical from which it secedes according to an operation of an acid is C(R1) (R2)-L-X.

[0032]

[Formula 8]

[0033] (R1, R2, L, and X are similarly defined in the above-mentioned formula (X1) among a formula.) L' expresses an alkylene group, a cyclo alkylene group, an arylene radical, or an aralkylene group.

[0034] The alkyl group in R1 and R2 is desirable, and the straight chain of carbon numbers 1-8, branching,

and an annular alkyl group are mentioned. Specifically, a methyl group, an ethyl group, a propyl group, i-propyl group, butyl, i-butyl, t-butyl, an amyl group, i-amyl group, t-amyl group, a hexyl group, a cyclohexyl radical, an octyl radical, a 2-ethylhexyl radical, etc. are mentioned. The alkyl group as R1 and R2 may have the substituent, can mention an aryl group, an amide group, an ureido radical, a urethane group, a hydroxy group, a carboxy group, a halogen atom, an alkoxy group, a thio alkoxy group, an acyl group, an acyloxy radical, an alkoxy carbonyl group, a cyano group, a nitro group, etc. as a substituent, and is 15 or less carbon number preferably.

[0035] As a divalent connection radical in L, although an alkylene group, an arylene radical, an aralkylene group, etc. are mentioned, you may have in them the radical further chosen from $-O-$, $-CO-$, $-CO_2-$, $-OSO-$, $-S-$, $-SO-$, and $-SO_2-$. As an alkylene group, preferably, carbon numbers 1-8 are caused, and the straight chain of carbon numbers 1-4 or the alkylene group of branching is mentioned preferably, for example, methylene, ethylene, a propylene, etc. are mentioned. as an arylene radical -- desirable -- carbon numbers 6-14 -- the arylene radical of carbon numbers 6-10 is mentioned more preferably, for example, a phenylene group is mentioned as a desirable thing. As an aralkylene group, preferably, carbon numbers 7-18 are caused, and the aralkylene group of carbon numbers 7-11 is mentioned preferably, for example, a phenylene methylene group and phenylene ethylene are mentioned as a desirable thing. These radicals may have substituents, such as a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1-4).

[0036] L' can mention the straight chain alkylene group of carbon numbers 2-10, the cyclo alkylene group of carbon numbers 6-14, the arylene radical of carbon numbers 6-14, or the aralkylene group of carbon numbers 7-15 preferably. What has the example [be / the same as that of L / it] of these radicals is mentioned. Moreover, you may have the substituent like L.

[0037] X -- a fluorine atom and a fluoro alkyl group -- at least -- the radical of either, alicycle structure, and ring structure which has either at least -- it is . As a fluoro alkyl group (alkyl group which has at least one fluorine atom) The alkyl group by which at least one hydrogen atom was permuted by the fluorine atom in the above-mentioned alkyl group as R1 and R2 can be mentioned. The alkyl group preferably permuted by the fluorine atom in at least one hydrogen atom in the straight chain of carbon numbers 1-8, branching, and an annular alkyl group can be mentioned. For example, a fluoro methyl group, difluoromethyl group, a trifluoromethyl radical, a fluoro ethyl group, a difluoro ethyl group, a trifluoroethyl radical, a pentafluoro ethyl group, the perfluoroalkyl radical of the other carbon numbers 1-8, etc. are mentioned, and it is a trifluoromethyl radical especially preferably. As alicycle structure in X, a monocycle mold may be used and a polycyclic mold may be used. As a monocycle mold, the cycloalkyl radical of carbon numbers 3-8 is mentioned preferably, for example, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, cyclo butyl, a cyclo octyl radical, etc. can be mentioned. As a polycyclic mold, the cycloalkyl radical of 6-20 carbon numbers is mentioned preferably, for example, an adamantyl radical, a norbornyl radical, an isoboronil radical, a camphor nil radical, a JISHIKURO pentyl radical, alpha-PINERU radical, a tricyclo deca nil radical, the tetracyclo dodecyl, a loss TANIRU radical, etc. can be mentioned. In addition, some carbon atoms in a cycloalkyl radical may be permuted by hetero atoms, such as an oxygen atom. As ring structure in X, the thing of carbon numbers 4-14 is desirable, for example, the benzene ring, a naphthalene ring, and an anthracene ring are mentioned. Moreover, you may be the hetero ring which has an oxygen atom, a sulfur

atom, and a nitrogen atom in endocyclic. As an example of a hetero ring, a furan ring, a thiophene ring, etc. are mentioned, for example.

[0038] These alicycle and rings may have the substituent and an alkyl group (preferably carbon numbers 1-4), an alkoxy group (preferably the carbon numbers 1-8, more preferably a carbon number 1 or 2), a hydroxyl group, a nitro group, a cyano group, a halogen atom, etc. are mentioned. The radical which has polarities, such as a methoxy group, a hydroxyl group, and a cyano group, preferably especially is excellent in adhesion with a substrate, and desirable.

[0039] In X, the fluorine atom or the fluoro alkyl group may be coupled directly with alicycle structure or ring structure, and may be combined through a connection radical. The radical mentioned as a connection radical as L which can be set a formula (X1), for example can be mentioned.

[0040] The thing of the following structure is mentioned as a desirable radical of Above X.

[Formula 9]

[0041] (AC expresses alicycle structure among a formula.) n expresses the integer of 1-3. L is synonymous with the thing in a formula (X1). As an example of X, the thing of the following structure is mentioned more preferably.

[Formula 10]

[0042] (M expresses single bond or a double bond among a formula.) even if G1 and G2 are the same, they may differ from each other, and they express a hydrogen atom, a fluorine atom, a fluoro alkyl group, a cyano group, or a hydroxyl group. The fluoro alkyl group is synonymous with the fluoro alkyl group which Above X has as G1 and G2. n expresses 0 or 1.

[0043] The following structure is mentioned as a polymerization nature repeat unit which has these.

[Formula 11]

(A expresses among a formula the radical chosen from a hydrogen atom, a methyl group, a cyano group, a trifluoromethyl radical, a fluorine atom, a chlorine atom, and a bromine atom.) R1, R2, L, and X are similarly defined in the above-mentioned formula (X1). n expresses 0 or 1. L' is similarly defined in the above (X2).

[0044] Although the example of a repeat unit of having the above-mentioned general formula (X1) or (X2) the radical expressed is shown hereafter, it does not limit to these.

[0045]

[Formula 12]

[0046]

[Formula 13]

[0047]

[Formula 14]

[0048]

[Formula 15]

[0049]

[Formula 16]

[0050] As for the resin (a) of this invention, it is also desirable to contain the repeat unit chosen from following repeat unit (Z1) – (Z3) in order to adjust dissolution contrast.

[0051]

[Formula 17]

[0052] (A expresses among a formula the radical chosen from a hydrogen atom, a methyl group, a fluorine atom, a bromine atom, a trifluoromethyl radical, and a cyano group.) Q expresses a hydrogen atom, an alkyl group, an aralkyl radical, or an aryl group. In addition, although Q may be acidolysis nature, both a fluorine atom and cyclic structure are not simultaneously included in Q in that case. n expresses 0 or 1.

[0053] Here, as an alkyl group as Q, the straight chain of carbon numbers 1–25, branching, and an annular alkyl group are mentioned preferably. For example, the straight chains and branching alkyl groups of carbon numbers 1–10, such as a methyl group, an ethyl group, a propyl group, i-propyl group, butyl, i-butyl, t-butyl, an amyl group, i-amyl group, t-amyl group, a hexyl group, an octyl radical, and a 2-ethylhexyl radical, and the alkyl group which has the alicycle structure shown by X are desirable. As an aralkyl radical, it is the aralkyl radical of carbon numbers 6–11 preferably, for example, benzyl, a phenethyl radical, a phenylpropyl radical, etc. are mentioned, and especially benzyl and a phenethyl radical are desirable. as an aryl group, the aryl group of carbon numbers 6–14 comes out preferably, and it is, for example, a phenyl group, a tolyl group, a dimethylphenyl radical, 2 and 4, 6-trimethyl phenyl radical, a naphthyl group, an anthryl radical, etc. can be mentioned. In addition, Q may have the substituent.

[0054] (A) The resin of a component may carry out the polymerization of other polymerization nature monomers in addition to the above-mentioned repeat unit.

[0055] What is shown below is contained as a copolymerization monomer which can be used together. For example, it is the compound which has one addition polymerization nature unsaturated bond chosen from acrylic ester other than the above, acrylamides, methacrylic ester, methacrylamide, an allyl compound, vinyl ether, vinyl ester, styrene, and crotonic-acid ester.

[0056] Specifically For example, acrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1–10) acrylate for example, a methyl acrylate, an ethyl acrylate, and acrylic-acid propyl — Acrylic-acid t-butyl, acrylic-acid amyl, acrylic-acid cyclohexyl, Acrylic-acid ethylhexyl, acrylic-acid octyl, acrylic-acid-t-octyl, Chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, Aryl acrylate (for example, phenyl acrylate etc.), such as pentaerythritol monoacrylate, glycidyl acrylate, benzyl acrylate, furfuryl acrylate, and tetrahydrofurfuryl acrylate;

[0057] Methacrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1–10) methacrylate for example, methyl methacrylate, ethyl methacrylate, and propyl methacrylate — Isopropyl methacrylate, t-butyl methacrylate, amyl methacrylate, Hexyl methacrylate, cyclohexyl

methacrylate, benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2 and 2-dimethyl-3-hydroxypropyl methacrylate, trimethylol propane mono-methacrylate, Pentaerythritol mono-methacrylate, glycidyl methacrylate, Aryl methacrylate (for example, phenyl methacrylate, cresyl methacrylate, naphthyl methacrylate, etc.), such as furfuryl methacrylate and tetrahydrofurfuryl methacrylate;

[0058] Acrylamides, for example, acrylamide, N-alkyl acrylamide (as an alkyl group), there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, benzyl, a hydroxyethyl radical, benzyl, etc. N-aryl acrylamide (as an aryl group, there are a phenyl group, a tolyl group, a nitrophenyl group, a naphthyl group, a cyanophenyl radical, a hydroxyphenyl radical, a carboxyphenyl radical, etc., for example.) N and N-dialkyl acrylamide (as an alkyl group) there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc. N and N-diaryl acrylamide (as an aryl group, there is a phenyl group etc., for example.) N-methyl-N-phenyl acrylamide, N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc.;

[0059] Methacrylamide, for example, methacrylamide, N-alkyl methacrylamide (as an alkyl group) there are the thing of the carbon atomic numbers 1-10, for example, a methyl group, an ethyl group, t-butyl, an ethylhexyl radical, a hydroxyethyl radical, a cyclohexyl radical, etc. N-aryl methacrylamide (there is a phenyl group etc. as an aryl group.) N and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group.) N and N-diaryl methacrylamide (there is a phenyl group etc. as an aryl group.) N-hydroxyethyl-N-methyl methacrylamide, N-methyl-N-phenyl methacrylamide, N-ethyl-N-phenyl methacrylamide etc.; An allyl compound For example, allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.;

[0060] vinyl ether (for example, hexyl vinyl ether --), for example, alkyl vinyl ether Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, The 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, Dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, Butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc., Vinyl aryl ether (for example, vinyl phenyl ether, the vinyl tolyl ether, vinyl KURORU phenyl ether, vinyl -2, 4-dichloro phenyl ether, the vinyl naphthyl ether, the vinyl anthranil ether, etc.);

[0061] Vinyl ester, for example, vinyl butyrate, vinyl iso butyrate, Vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, Vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, Vinyl methoxy acetate, vinyl butoxy acetate, vinyl phenyl acetate, Vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, benzoic-acid vinyl, salicylic acid vinyl, Krol benzoic-acid vinyl, tetra-KURORU benzoic-acid vinyl, naphthoic-acid vinyl, etc.;

[0062] styrene, for example, styrene, and alkyl styrene (for example, methyl styrene --) Dimethyl styrene, trimethyl styrene, ethyl styrene, diethyl styrene, Isopropyl styrene, butyl styrene, hexyl styrene, cyclohexyl styrene, DESHIRU styrene, benzyl styrene, KURORU methyl styrene, trifluormethyl styrene, Alkoxy styrene,

such as ethoxy methyl styrene and acetoxy methyl styrene for example, methoxy styrene and 4-methoxy-3-methyl styrene -- halogen styrene (for example, KURORU styrene --), such as dimethoxy styrene Dichloro styrene, TORIKURORU styrene, tetra-KURORU styrene, pen TAKURORU styrene, bromine styrene and a jib -- carboxy styrene, such as ROM styrene, iodine styrene, Fluor styrene, Tori Fluor styrene, 2-bromine-4-trifluormethyl styrene, and 4-Fluor-3-trifluormethyl styrene, and vinyl naphthalene; [0063] Crotonic-acid ester (for example, dimethyl itaconate, itaconic-acid diethyl, dibutyl itaconate, etc.), for example, crotonic-acid alkyl (for example, crotonic-acid butyl, crotonic-acid hexyl, glycerol mono-crotonate, etc.); itaconic-acid dialkyls,; there are the dialkyl ester of a maleic acid or boletic acid, maleic anhydrides (for example, dimethyl MARERETO, dibutylfumarate, etc.), maleimide, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc. In addition, generally what is necessary is just a copolymerizable addition polymerization nature unsaturated compound.

[0064] Especially, they are the acrylonitrile from a viewpoint with a transparency of 157nm, a methacrylonitrile, and alpha-trifluoro acrylic-acid alkyl ester (in addition, as an alkyl group, it is the straight chain, branching, or the annular alkyl group of carbon numbers 1-10 preferably, and the alkyl group which a part or all of a hydrogen atom of an alkyl group is permuted by the fluorine atom, or contains a cyclic-hydrocarbon radical is mentioned still more preferably.). An operation of an acid may decompose these alkyl groups. Moreover, the alkyl group may have the substituent and can mention a hydroxy group, a carboxy group, a halogen atom, an alkoxy group, a cyano group, etc. as a substituent. It is desirable.

[0065] (A) the content of the repeat unit which contains the structure expressed with a general formula (X1) in the resin of a component -- general -- 10-80-mol % -- desirable -- 20-70-mol % -- it is 30-60-mol % still more preferably. (A) the content of the repeat unit which contains the structure expressed with a general formula (X2) in the resin of a component -- general -- 5-50-mol % -- desirable -- 5-40-mol % -- it is 10-30-mol % still more preferably. (A) the repeat unit containing the structure which may include both repeat units which contain the structure expressed with a general formula (X1) and a general formula (X2) in the resin of a component, and is expressed with a general formula (X1) and a general formula (X2) in that case -- the sum total -- it is -- 10-70-mol % -- desirable -- 15-60-mol % -- it is 20-50-mol % still more preferably. (A) the time of containing repeat unit (Z1) - (Z3) in the resin of a component -- as a repeat unit (Z1) - (Z3) a total amount -- general -- 5-80-mol % -- desirable -- 10-70-mol % -- it is 20-50-mol % still more preferably.

[0066] The repeat structural unit expressed with the above-mentioned example may be respectively used by one sort, and plurality may be mixed and used for it. The above-mentioned resin is compoundable by the usual radical polymerization method. The desirable molecular weight of the resin (A) of this invention which has the above-mentioned repeat structural unit is 1,000-200,000 in a weighted mean, and is used in 3,000-20,000 still more preferably. molecular weight distribution (weight average molecular weight/number average molecular weight) -- usually -- 1-10 -- it is -- desirable -- 1-3 -- the thing of the range of 1-2 is used still more preferably. The smaller thing of a molecular weight distribution has resolution, a resist configuration, and the more smooth side attachment wall of a resist pattern, and is excellent in roughness nature.

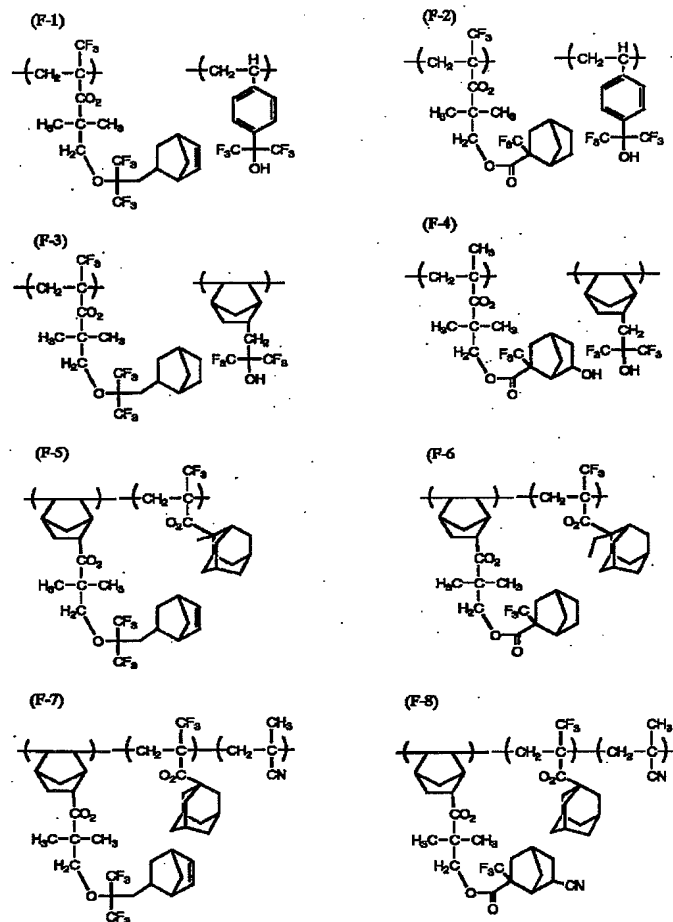
[0067] Generally the addition of the resin (A) of this invention is preferably used in 90 - 98% of the weight of the range still more preferably 80 to 99% of the weight 50 to 99.5% of the weight on the basis of the total

solids of a constituent.

[0068] Although the example of resin is given to below, it does not limit to these.

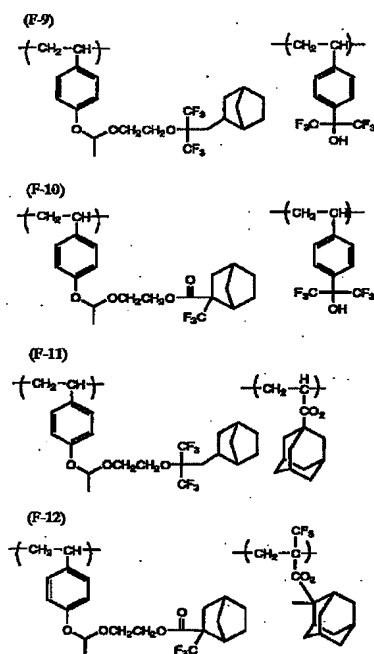
[0069]

[Formula 18]



[0070]

[Formula 19]



[0071] [2] The compound which generates an acid by the exposure of an activity beam of light or a radiation (B component)

The positive-resist constituent of this invention contains especially an activity beam of light or a radiation, and the compound that generates an acid by the exposure of F2 excimer-laser light. It can choose from the compounds currently used as a compound (photo-oxide generating agent) which decomposes by the exposure of an activity beam of light or a radiation, and generally generates an acid by the exposure of an activity beam of light or a radiation as a compound which generates an acid. That is, it can be used, choosing from the compounds which generate an acid by a well-known light (400–200nm ultraviolet rays, far ultraviolet rays, especially preferably g line, h line, i line, KrF excimer laser light) currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, ArF excimer laser light, F2 excimer-laser light, the electron ray, the X-ray, the molecular beam, or the ion beam, and those mixture suitably.

[0072] as such a compound — for example — S.I.Schlesinger, *Photogr.Sci.Eng.*, 18, and 387 (1974) — Diazonium salt given in T.S.Bal et al, *Polymer*, 21, 423 (1980), etc., U.S. Pat. No. 4,069,055, said 4,069,056 numbers, ** Re No. 27,992, Ammonium salt given in JP,3-140140,A etc., D.C.Necker et al, *Macromolecules*, 17, 2468 (1984), C.S.Wen et al, *Teh, Proc.Conf.Rad.Curing ASIA*, p478 Tokyo, Oct (1988), Phosphonium salt given in U.S. Pat. No. 4,069,055, said 4,069,056 numbers, etc., J.V.Crivello et al, *Macromolecules*, 10 (6), 1307 (1977), *Chem.& Eng.News*, Nov.28, p31 (1988), The Europe patent No. 104,143, said 339,049 numbers, 410,201, Iodonium salt given in JP,2-150848,A, JP,2-296514,A, etc., J.V.Crivello et al, *Polymer J.* 17, 73 (1985), J.V.Crivello et al., *J.Org.Chem.*, 43, 3055 (1978), W.R.Watt et al, *J.Polymer Sci., PolymerChem.Ed.*, 22, 1789 (1984), J.V.Crivello et al, *Polymer Bull.*, 14, 279 (1985), J.V.Crivello et al, *Macromolecules*, 14 (5), 1141 (1981), J.V.Crivello et al, *J.Polymer Sci., Polymer Chem.Ed.*, 17, 2877 (1979), The Europe patent No. 370,693, said 161,811 numbers, said 410,201 numbers, said — No. 339,049 — said — No. 233,567 — said — No.

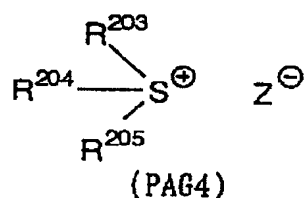
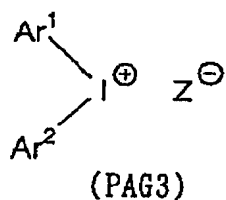
297,443 -- said -- No. 297,442 U.S. Pat. No. 4,933,377, said 3,902,114 numbers, said 4,760,013 numbers, Said 4,734,444 numbers, said 2,833,827 numbers, the Germany patent No. 2,904,626, Sulfonium salt given in said 3,604,580 numbers, said 3,604,581 numbers, etc., J.V.Crivello et al, *Macromolecules*, 10 (6), A seleno NIUMU salt given in 1307 (1977), J.V.Crivello et al, *J.Polymer Sci., Polymer Chem.Ed.*, 17, 1047 (1979), etc., Onium salt, such as arsonium salt given in C.S.Wen et al, *Teh, Proc.Conf.Rad.Curing ASIA*, p478 Tokyo, Oct (1988), etc., U.S. Pat. No. 3,905,815, JP,46-4605,B, JP,48-36281,A, JP,55-32070,A, JP,60-239736,A, JP,61-169835,A, JP,61-169837,A, JP,62-58241,A, JP,62-212401,A, An organic halogenated compound given in JP,63-70243,A, JP,63-298339,A, etc., K.Meier et al, *J.Rad.Curing*, 13 (4), 26 (1986), T.P.Gill et al, *Inorg.Chem.*, 19, 3007 (1980), D.Astruc, *Acc.Chem.Res.*, 19 (12), An organic metal / organic halogenide given in 377 (1896), JP,2-161445,A, etc., S.Hayase et al, *J.Polymer Sci.*, 25,753 (1987), E. Reichmanis et al, *J.PolymerSci., Polymer Chem.Ed.*, 23, 1 (1985), Q.Q.Zhu et al, *J.Photochem.*, 36, 85, 39, 317 (1987), B.Amit et al, *Tetrahedron Lett.*, (24) 2205 (1973), D.H.R.Barton et al, *J.Chem Soc.*, 3571 (1965), P.M.Collins et al, *J.Chem.Soc., Perkin I*, 1695 (1975), M.Rudinstein et al and *Tetrahedron Lett.*, (17), 1445 (1975), J.W.Walker et al, *J.Am.Chem.Soc.*, 110, 7170 (1988), S.C.Busman et al, *J.Imaging Technol.*, 11 (4), 191 (1985), H.M.Houlihan et al, *Macromolecules*, 21, 2001 (1988), P.M.Collins et al, *J.Chem.Soc., Chem.Comm.*, 532 (1972), S.Hayase et al, *Macromolecules*, 18, 1799 (1985), E.Reichmanis et al, *J.Electrochem.Soc., Solid State Sci.Technol.*, 130 (6), F.M.Houlihan et al, *Macromolecules*, 21, 2001 (1988), the Europe patent 0290th, and No. 750 -- said -- No. 046 or 083 -- said -- No. 156 or 535 -- said -- 271 No. 851, said 0,388,343 numbers, U.S. Pat. No. 3,901,710, The photo-oxide generating agent which has 0-nitrobenzyl mold protective group of a publication in said 4,181,531 numbers, JP,60-198538,A, JP,53-133022,A, etc., M. TUNOOKA et al, *Polymer Preprints Japan*, 35 (8), G.Berner et al, *J.Rad.Curing*, 13 (4), W.J.Mijs et al, *Coating Technol.*, 55 (697), 45 (1983), Akzo, H.Adachi et al, *Polymer Preprints, Japan*, 37 (3), the Europe patent 0199th and No. 672 -- said -- No. 84515 -- said -- No. 044 or 115 said -- No. 618,564 -- said -- No. 0101 or 122 and U.S. Pat. No. 4,371,605 -- said -- 4,431,774 a number, JP,64-18143,A, and JP,2-245756,A -- The disulfon compound of a publication etc. can be mentioned to a compound which photodissociates and generates a sulfonic acid, JP,61-166544,A, etc. which are represented by imino sulfonate given in JP,3-140109,A etc.

[0073] In this invention, the compound (B1) which generates an organic sulfonic acid by the exposure of an activity beam of light or a radiation is desirable as a compound which generates an acid by the exposure of an activity beam of light or a radiation. As a compound (B1) which generates an organic sulfonic acid by the exposure of an activity beam of light or a radiation, the compound (B1a) which generates a fluorine content sulfonic acid by the exposure of an activity beam of light or a radiation, and the compound (B1b) which generates fluorine a non-containing sulfonic acid by the exposure of an activity beam of light or a radiation can be mentioned.

[0074] [B1a] As a compound which generates a fluorine content sulfonic acid by the exposure of the compound activity beam of light or radiation which generates a fluorine content sulfonic acid by the exposure of an activity beam of light or a radiation, the iodonium salt expressed with the following general formula (PAG3) or the sulfonium salt expressed with a general formula (PAG4) can be mentioned, for example.

[0075]

[Formula 20]



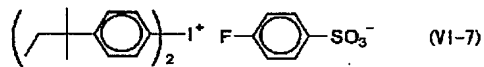
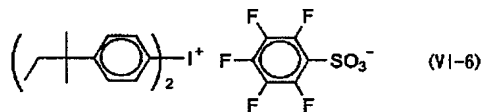
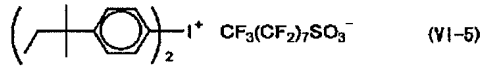
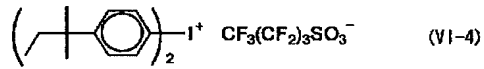
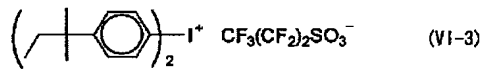
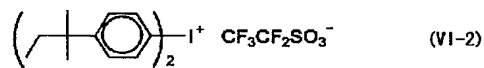
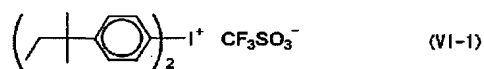
[0076] Ar1 and Ar2 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R203, R204, and R205 show respectively the alkyl group which is not permuted [a permutation or] and an aryl group independently. Z⁻ shows the sulfonic-acid anion which has at least one fluorine atom. Moreover, two, and Ar1 and Ar2 of R203, R204, and R205 may be combined through each single bond or substituent. As an aryl group as Ar1, Ar2, R203, R204, and R205, it is the alkyl group of carbon numbers 1-8 preferably [it is desirable and] as the aryl group of carbon numbers 6-14, and an alkyl group. As a desirable substituent, to an aryl group, it is the alkoxy group of carbon numbers 1-8, the alkyl group of carbon numbers 1-8, the alkoxy carbonyl group of carbon numbers 2-9, the alkyl carbonylamino radical of carbon numbers 2-9, a nitro group, a carboxyl group, a hydroxy group, a halogen atom, and a phenylthio radical, and the alkoxy group of carbon numbers 1-8, the aryl group of carbon numbers 5-14, the aryl carbonyl group of carbon numbers 6-15, a carboxyl group, and a halogen atom can be mentioned to an alkyl group.

[0077] As a sulfonic-acid anion of Z⁻, the aliphatic hydrocarbon of the carbon numbers 1-20 which have at least one fluorine atom, and the aromatic hydrocarbon of carbon numbers 5-20 can be mentioned preferably. These may have the substituent and can mention as a substituent the alkoxy group in which carbon numbers 1-10 may be carrying out the fluorine permutation, the alkoxy carbonyl group in which carbon numbers 2-11 may be carrying out the fluorine permutation, a phenylamino radical, a phenyl carbonyl group, a halogen atom, and a hydroxyl group, for example. To aromatic hydrocarbon, the alkyl group of carbon numbers 1-15 can be mentioned further. In addition, especially about an aliphatic series sulfonic-acid anion, the anion which has a fluorine atom on alpha carbon atom of a sulfonic acid has high acid strength, and is in the inclination to perform salt exchange easily to the anion which does not have a fluorine atom. Moreover, a perfluoro aliphatic series sulfonic acid has still higher acid strength.

[0078] Although an example is given to below, it is not limited to these.

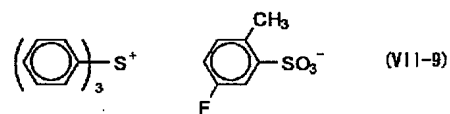
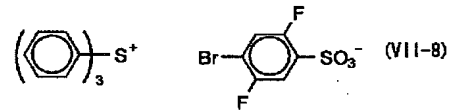
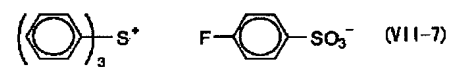
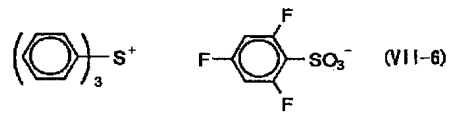
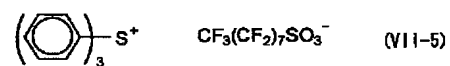
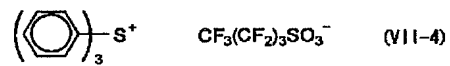
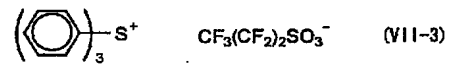
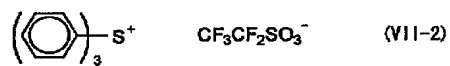
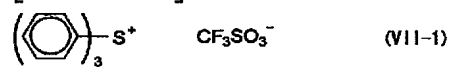
[0079]

[Formula 21]



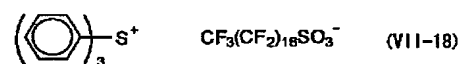
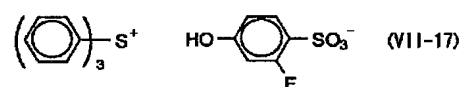
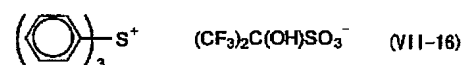
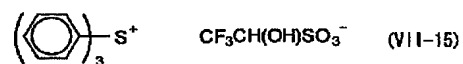
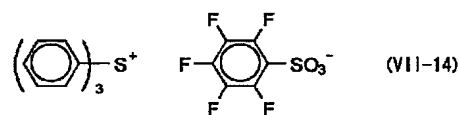
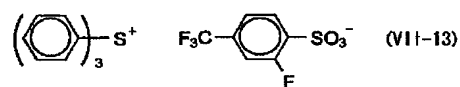
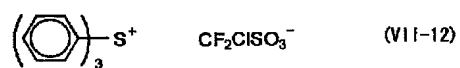
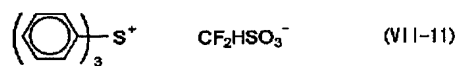
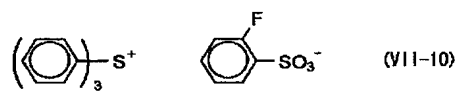
[0080]

[Formula 22]



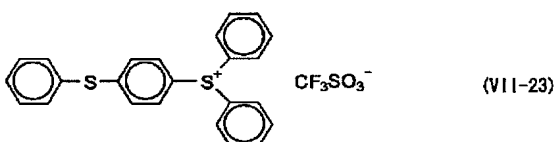
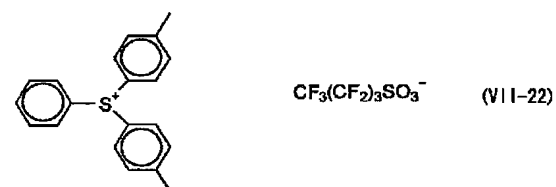
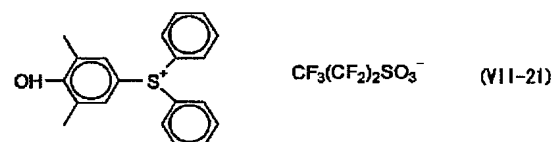
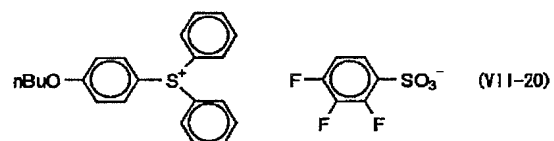
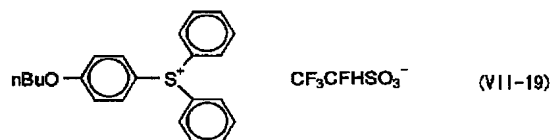
[0081]

[Formula 23]



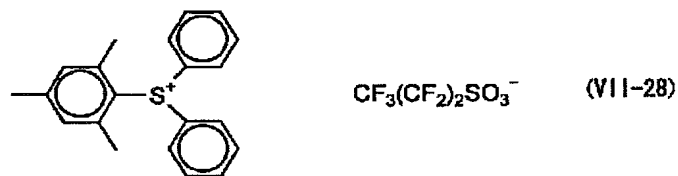
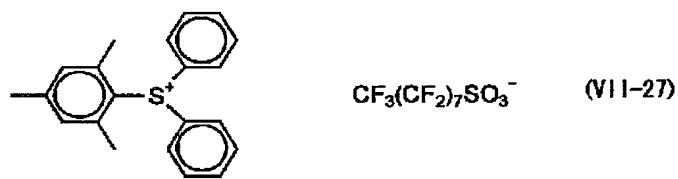
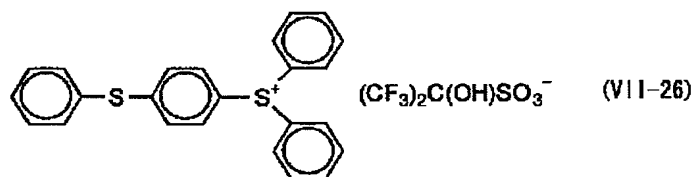
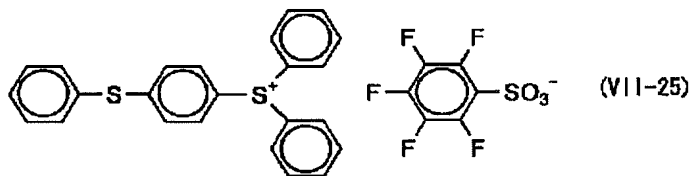
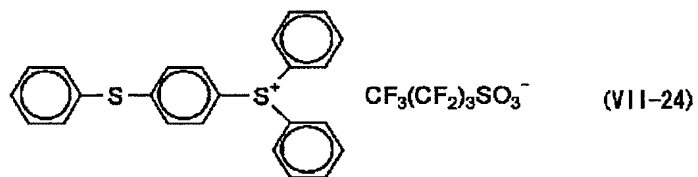
[0082]

[Formula 24]



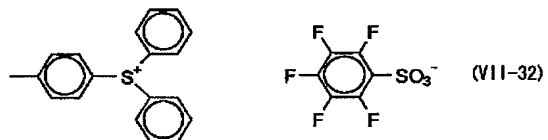
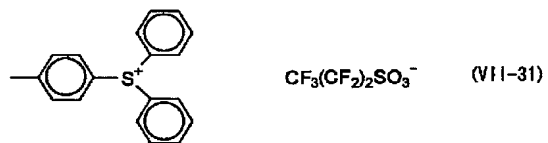
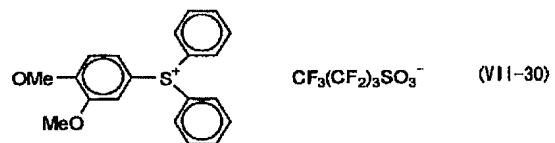
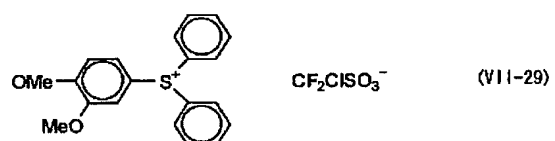
[0083]

[Formula 25]



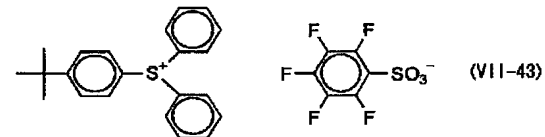
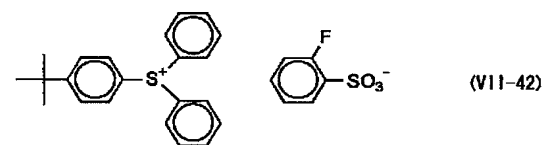
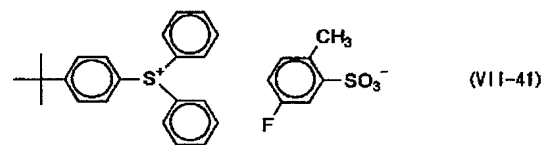
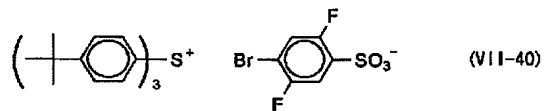
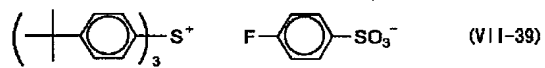
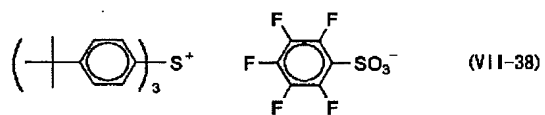
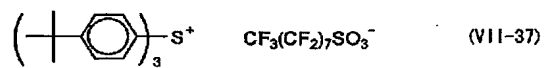
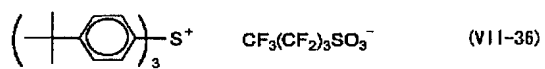
[0084]

[Formula 26]



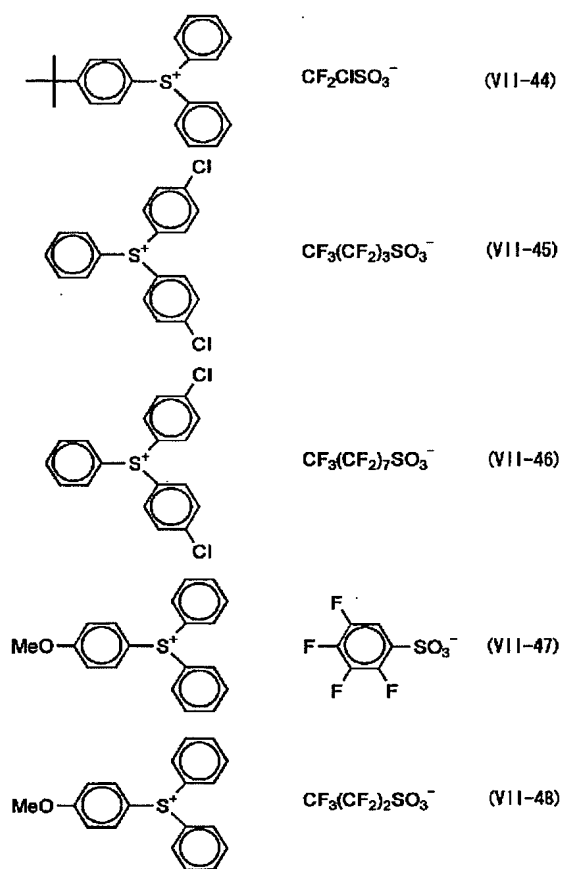
[0085]

[Formula 27]



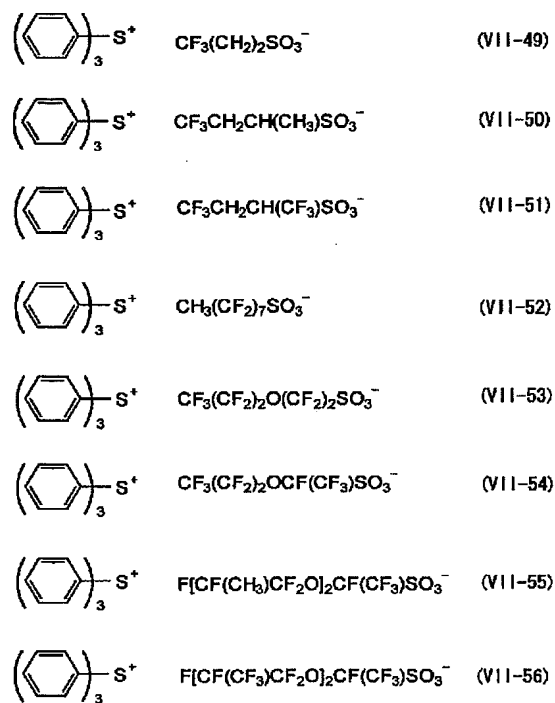
[0086]

[Formula 28]



[0087]

[Formula 29]

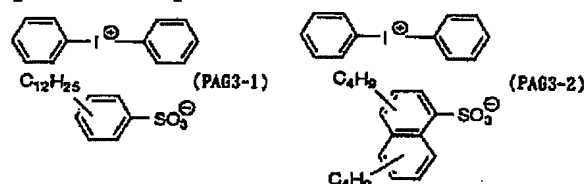


[0088] [B1b] As a compound which generates fluorine a non-containing sulfonic acid by the exposure of the compound activity beam of light or radiation which generates fluorine a non-containing sulfonic acid by the exposure of an activity beam of light or a radiation, the iodonium salt and sulfonium salt which are a previous general formula (PAG3) and (PAG4) the sulfonic-acid anion in which it sets and Z- does not have a fluorine atom can be mentioned, for example.

[0089] Although the compound shown below as an example is mentioned, it is not limited to these.

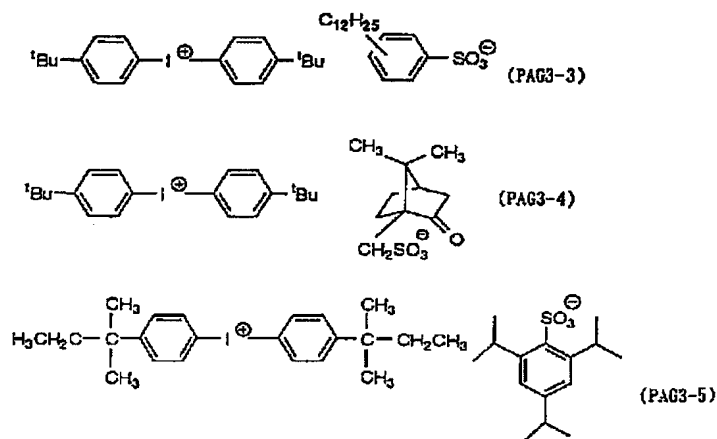
[0090]

[Formula 30]



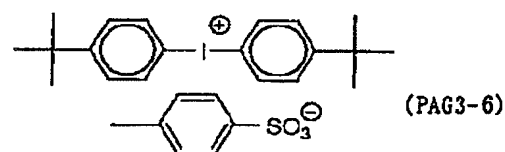
[0091]

[Formula 31]



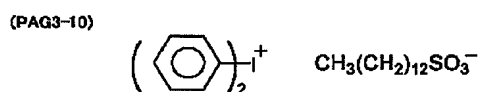
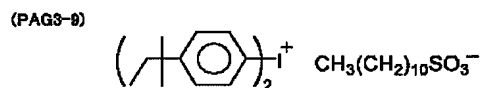
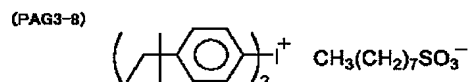
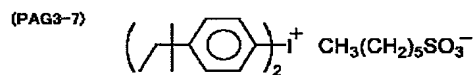
[0092]

[Formula 32]



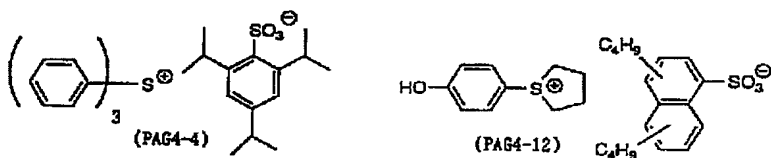
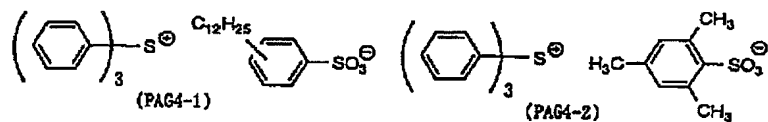
[0093]

[Formula 33]



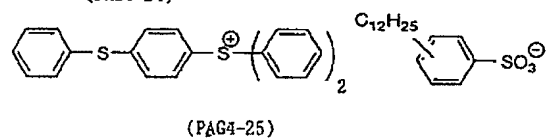
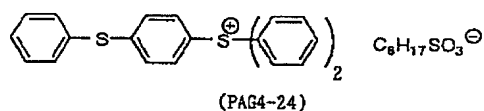
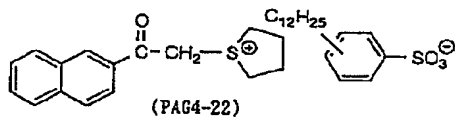
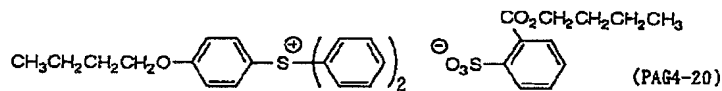
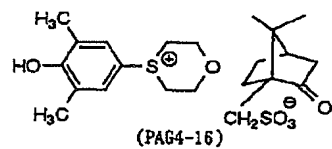
[0094]

[Formula 34]



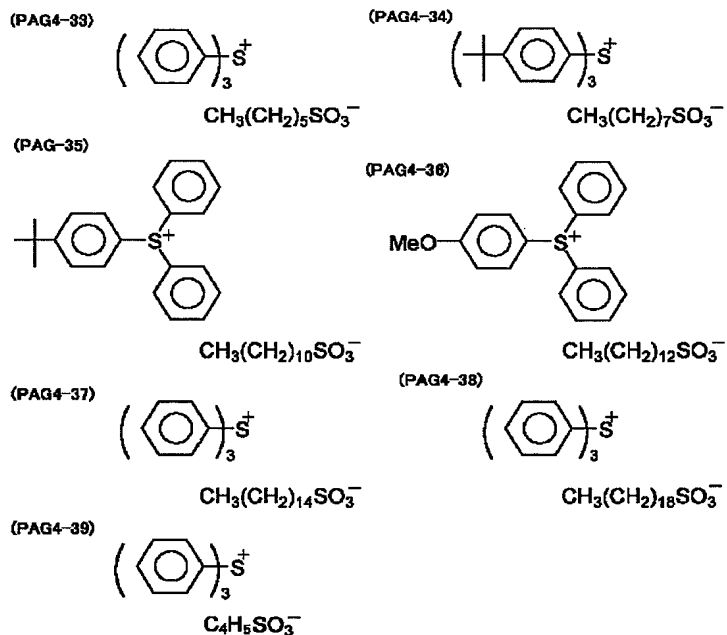
[0095]

[Formula 35]



[0096]

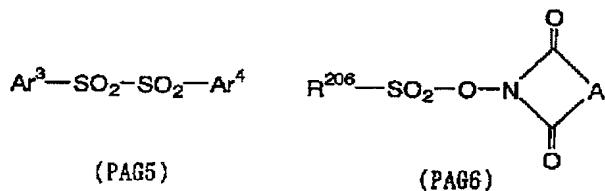
[Formula 36]



[0097] Moreover, the imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5) can be mentioned.

[0098]

[Formula 37]

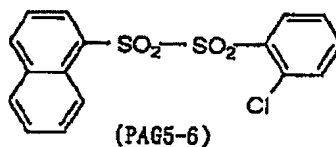
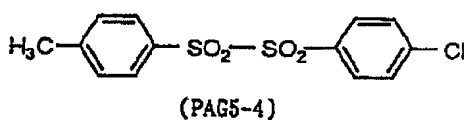
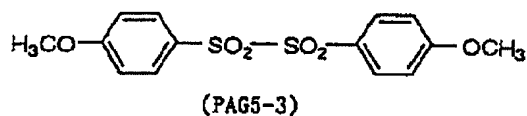
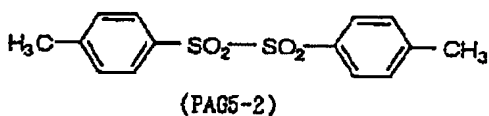
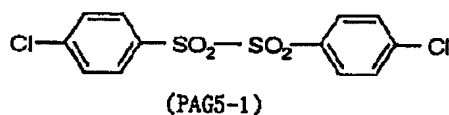


[0099] Ar3 and Ar4 show respectively the aryl group which is not permuted [a permutation or] independently among a formula. R206 shows the alkyl group which is not permuted [a permutation or] and an aryl group. A shows the alkylene group which is not permuted [a permutation or], an alkenylene group, and an arylene radical.

[0100] Although the compound shown below as an example is mentioned, it is not limited to these.

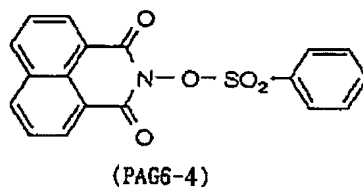
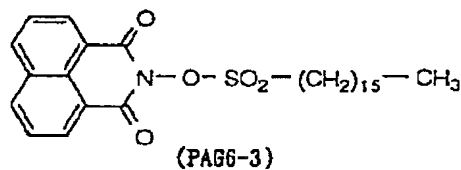
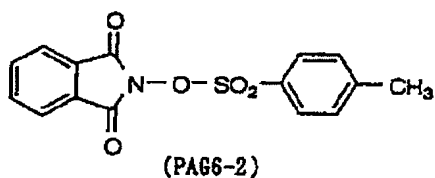
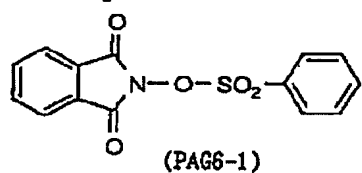
[0101]

[Formula 38]



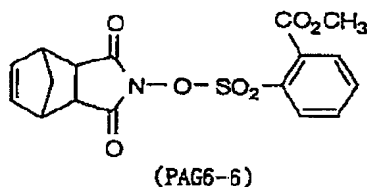
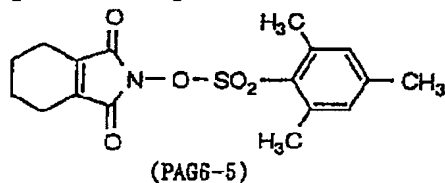
[0102]

[Formula 39]



[0103]

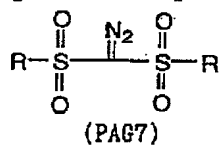
[Formula 40]



[0104] Moreover, the diazo disulfon derivative expressed with the following general formula (PAG7) can be mentioned.

[0105]

[Formula 41]

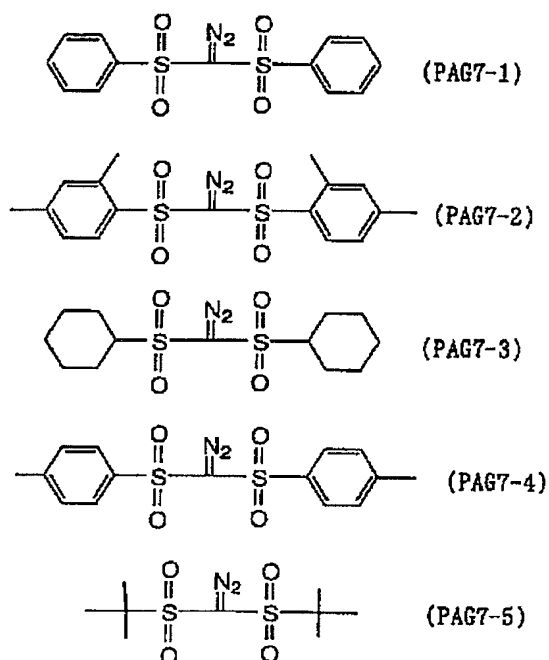


[0106] R expresses among a formula a straight chain, branching, an annular alkyl group, or the aryl group that may be permuted.

[0107] Although the compound shown below as an example is mentioned, it is not limited to these.

[0108]

[Formula 42]



[0109] The compound of the above [B1a] and [B1b] can make an aromatic compound able to react using a periodate, and can compound the obtained iodonium salt by carrying out salt exchange to a corresponding sulfonic acid. Moreover, the phenyl sulfoxide which is not permuted [aryl Grignard reagents such as aryl magnesium bromide, a permutation, or] is made to react, and the obtained triarylsulfonium halide can be compounded by the approach of carrying out salt exchange with a corresponding sulfonic acid. Moreover, condensation, the approach of carrying out salt exchange, a diaryl iodonium salt, and a diaryl sulfide are [the phenyl sulfoxide which is not permuted / a permutation or / and a corresponding aromatic compound] compoundable by condensation, the approach of carrying out salt exchange, etc. using the catalyst of copper acetate etc. using acid catalysts, such as methansulfonic acid / diphosphorus pentoxide, or an aluminum chloride. Once leading salt exchange to a halide salt, it can carry out salt exchange also of also using the approach of using silver reagents, such as a silver oxide, and changing into a sulfonate, or ion exchange resin. Moreover, the sulfonic acid or sulfonate used for salt exchange can be obtained by hydrolysis of commercial sulfonic-acid halide etc., using a commercial thing.

[0110] In this invention, it is desirable to use the compound (B-2) which has a carboxylic acid as the compound which decomposes according to an operation of an acid and generates a carboxylic acid with the compound (B1) which generates an organic sulfonic acid by the exposure of an activity beam of light or a radiation, or an anion. As a compound (B-2) which has a carboxylic acid as the compound which decomposes according to an operation of an acid and generates a carboxylic acid, or an anion The compound which has a fluorine content carboxylic acid as the compound which decomposes according to an operation of an acid and generates a fluorine content carboxylic acid, or an anion (B-2a), The compound (B-2b) which has fluorine a non-containing carboxylic acid as the compound which decomposes according to an operation of an acid and generates fluorine a non-containing carboxylic acid, or an anion can be mentioned.

[0111] [B-2a] As an ionicity compound fluorine content carboxylic acid which has a fluorine content carboxylic acid as the compound which decomposes according to an operation of an acid and generates a fluorine content carboxylic acid, and an anion, the aliphatic carboxylic acid by which the fluorine permutation was carried out, and the aromatic carboxylic acid by which the fluorine permutation was carried out can be mentioned.

[0112] As aliphatic carboxylic acid by which the fluorine permutation was carried out, the fluorine permutation object of aliphatic carboxylic acid, such as an acetic acid, a propionic acid, n-butanoic acid, an isobutyric acid, valerianic acid, trimethylacetic acid, a caproic acid, oenanthalic acid, a caprylic acid, pelargonic acid, a capric acid, a lauryl acid, a myristic acid, a palmitic acid, stearin acid, undecanoic acid, dodecanoic acid, and a tridecanoic acid, is mentioned. These may have the hydroxyl group, the alkoxy group, and the halogen atom as a substituent. Moreover, what contains connection radicals, such as an oxygen atom, a sulfur atom, a carbonyl group, a carboxyl group, and a sulfonyl group, in the aliphatic series chain is desirable. What is expressed with the following general formula as desirable aliphatic carboxylic acid by which the fluorine permutation was carried out can be mentioned.

L expresses a hydrogen atom or a fluorine atom among an $L-(CH_2)_p(CF_2)_q(CH_2)_r-COOH$ general formula. p and r express the integer of 0-15, and q expresses the integer of 1-15 independently respectively. The hydrogen atom or fluorine atom of an alkyl chain in this general formula may be permuted by the alkyl group (preferably carbon numbers 1-5) which may be permuted by the fluorine atom, the alkoxy group (preferably carbon numbers 1-5) which may be permuted by the fluorine atom, or the hydroxyl group. It is desirable that the carbon number is the fluorine permutation object of 2-20, and the saturation aliphatic carboxylic acid that is 4-20 more preferably preferably as aliphatic carboxylic acid by which the fluorine permutation was carried out [above-mentioned]. By making this carbon number into four or more pieces, the diffusibility of the carboxylic-acid resolvability to generate falls and the line breadth change by the passage of time from exposure to afterbaking can be controlled more. Especially, the fluorine permutation object of the straight chain of 4-18 carbon numbers or branching saturation aliphatic carboxylic acid is desirable.

[0113] As an aromatic series group carboxylic acid by which the fluorine permutation was carried out, it is desirable that carbon numbers are 7-20, and the fluorine permutation object of the aromatic carboxylic acid which is 7-15 more preferably and is 7-11 still more preferably. Specifically, the fluorine permutation object of aromatic carboxylic acid, such as a benzoic acid, a permutation benzoic acid, a naphthoic acid, a permutation naphthoic acid, an anthracene carboxylic acid, and a permutation anthracene carboxylic acid (it is here and an alkyl group, an alkoxy group, a hydroxyl group, a halogen atom, an aryl group, an acyl group, an acyloxy radical, a nitro group, an alkylthio group, and an aryl thio radical are mentioned as a substituent), is mentioned. Especially, the fluorine permutation object of a benzoic acid and a permutation benzoic acid is desirable.

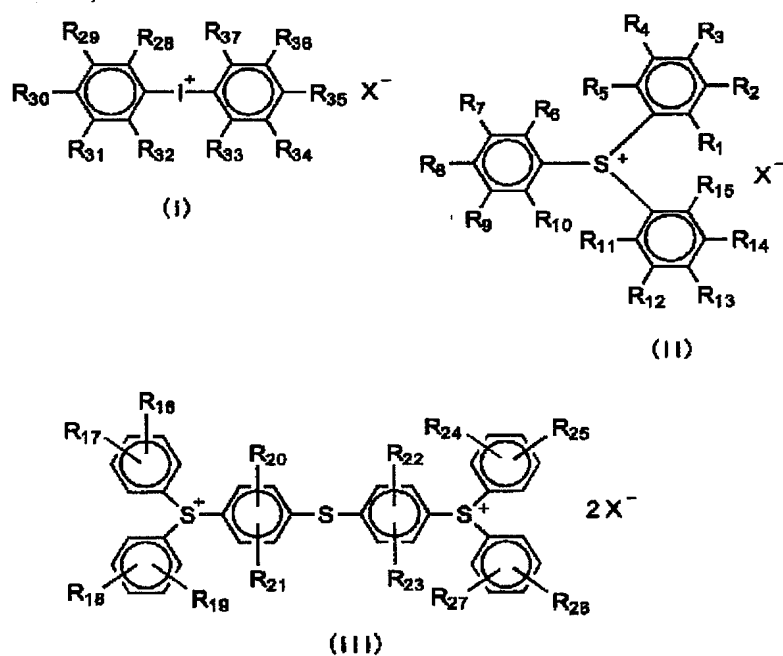
[0114] The carboxylic acid of the aliphatic series permuted by these fluorines atom or aromatic series is a carboxylic acid (perfluoro saturation aliphatic carboxylic acid or perfluoro aromatic carboxylic acid) of the aliphatic series by which one or more of the hydrogen atom which exists in frames other than a carboxyl group were permuted by the fluorine atom, and all the hydrogen atoms that exist in frames other than a carboxyl group preferably especially were permuted by the fluorine atom, or aromatic series. Thereby, sensibility comes to be further excellent. In addition, especially about an aliphatic-carboxylic-acid anion, the

anion which has a fluorine atom on alpha carbon atom of a carboxylic acid has high acid strength, and is in the inclination to perform salt exchange easily to the carboxylic-acid anion which does not have a fluorine atom. Moreover, perfluoro aliphatic carboxylic acid has still higher acid strength.

[0115] The onium salt compounds (sulfonium salt, iodonium salt, etc.) which have the anion of the carboxylic acid of the aliphatic series permuted by the above fluorine atoms or aromatic series as a counter anion as a compound which decomposes according to an operation of an acid and generates a fluorine content carboxylic acid, the imide carboxylate compound which has a carboxylate radical, or a nitrobenzyl ester compound is mentioned. The compound more preferably expressed with the following general formula (I) – (III) is mentioned. Thereby, sensibility, resolving power, and an exposure margin come to be further excellent. This compound generates the carboxylic acid of the saturation aliphatic series permuted by at least one fluorine atom which decomposes according to an operation of an acid and is equivalent to X^- of a general formula (I) – (III), or aromatic series.

[0116]

[Formula 43]



[0117] (R1 –R37 express a hydrogen atom, a straight chain, branching or an annular alkyl group, a straight chain, branching or an annular alkoxy group, a hydroxy group, a halogen atom, or 38 –S–R independently respectively among the above-mentioned formula.) R38 expresses a straight chain, branching, an annular alkyl group, or an aryl group here. X⁻ is the anion of the carboxylic acid of the aliphatic series permuted by at least one fluorine atom, or aromatic series.

X⁻ is the anion of perfluoro aliphatic carboxylic acid or perfluoro aromatic carboxylic acid preferably, and is the anion of the fluorine permutation alkyl carboxylic acid of four or more carbon numbers especially preferably.

[0118] The thing of 1–4 carbon numbers like a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, and t-butyl in a general formula (I) – (III) which may have a substituent as the straight chain of

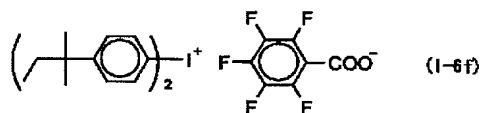
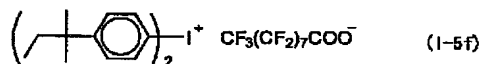
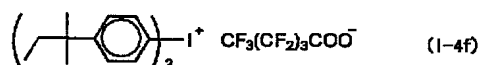
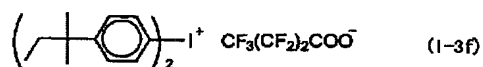
R1–R38 and a branching alkyl group is mentioned. As an annular alkyl group, the thing of 3–8 carbon numbers like a cyclopropyl group, a cyclopentyl group, and a cyclohexyl radical which may have a substituent is mentioned. As an alkoxy group of R1–R37, the thing of 1–4 carbon numbers like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n-butoxy radical, an iso butoxy radical, a sec-butoxy radical, and a t-butoxy radical is mentioned. As a halogen atom of R1–R37, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. As an aryl group of R38, the thing of 6–14 carbon numbers, such as a phenyl group, a tolyl group, a methoxyphenyl radical, and a naphthyl group, is mentioned. An aryl group may have a substituent. The alkoxy group of 1–4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, iodine atom), the aryl group of 6–10 carbon numbers, the alkenyl radical of 2–6 carbon numbers, a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. are mentioned preferably as these substituents.

[0119] The iodonium compound or sulfonium compound expressed with the general formula (I) used by this invention – (III) has the anion of the carboxylic acid of the saturation aliphatic series permuted by at least one fluorine atom, or aromatic series as the pair anion X⁻. These anions are anions (–COO⁻) from which the hydrogen atom of this carboxylic acid (–COOH) seceded.

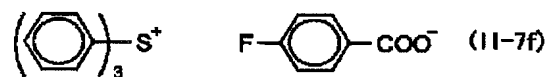
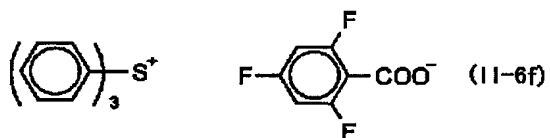
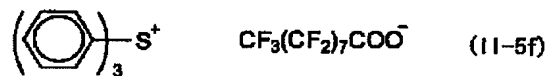
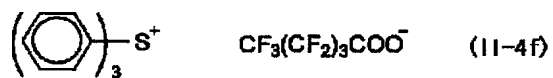
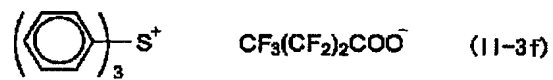
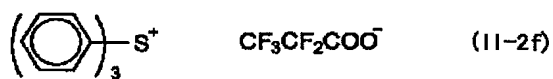
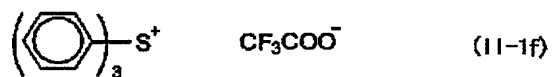
[0120] Although an example is shown below, this invention is not limited to these.

Example [of a compound] (I-1f) –expressed with a general formula (I) (I-36f) : [0121]

[Formula 44]

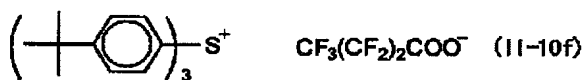


[0122] Example [of a compound] (II-1f) – expressed with a general formula (II) (II-67f): [Formula 45]



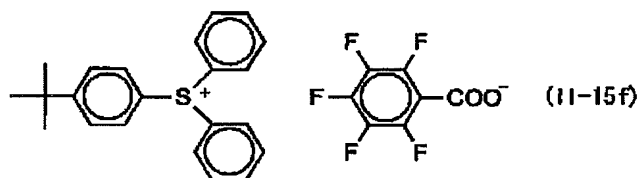
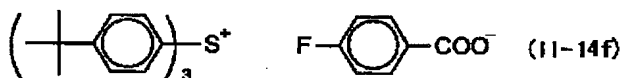
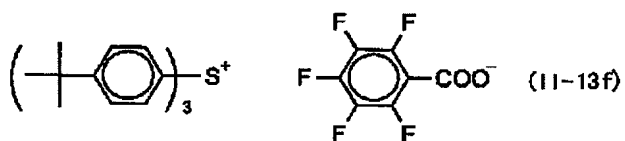
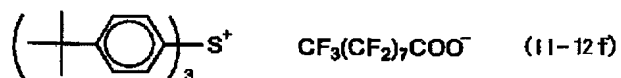
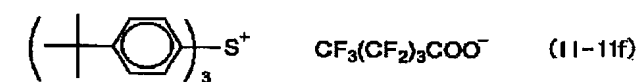
[0123]

[Formula 46]



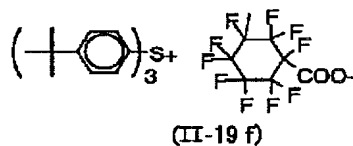
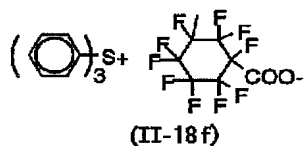
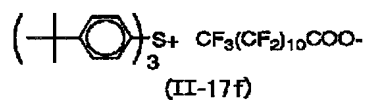
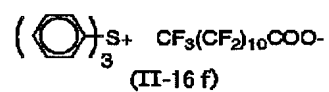
[0124]

[Formula 47]



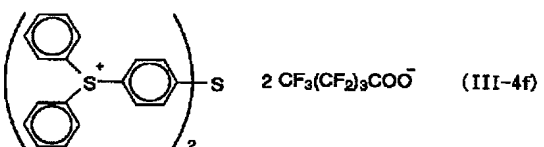
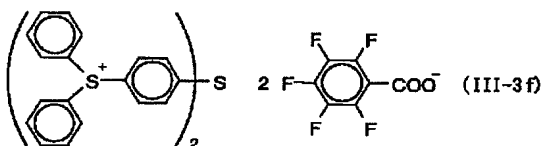
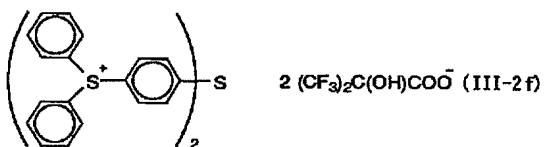
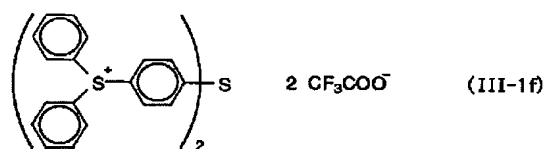
[0125]

[Formula 48]



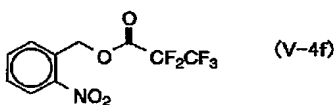
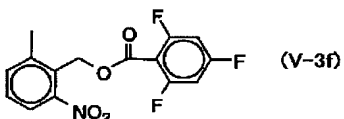
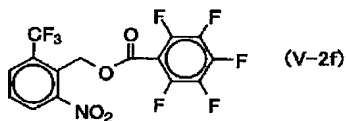
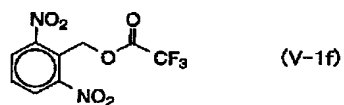
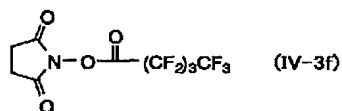
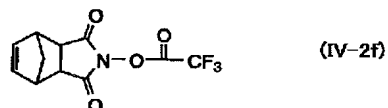
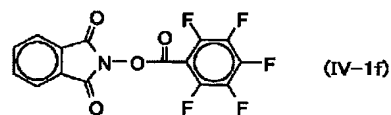
[0126] Example [of a compound] (III-1f) –expressed with a general formula (III) (III-4f) : [0127]

[Formula 49]



[0128] Example [of other compounds] (IV-1f) –(V-4f) : [0129]

[Formula 50]



[0130] The compound expressed with the above-mentioned general formula (I) can make an aromatic

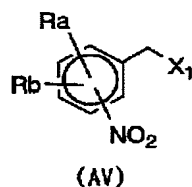
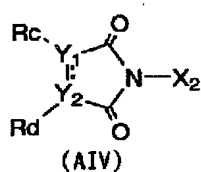
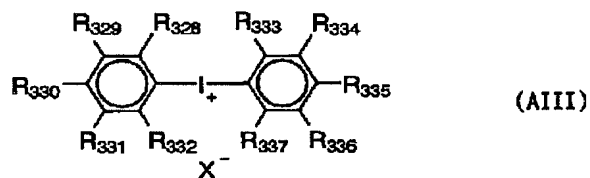
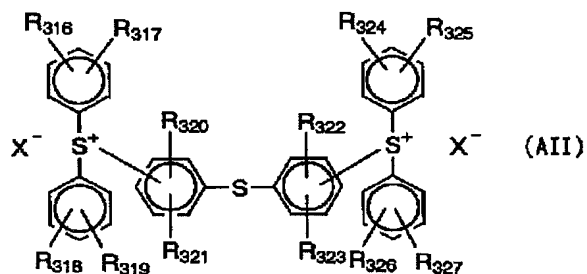
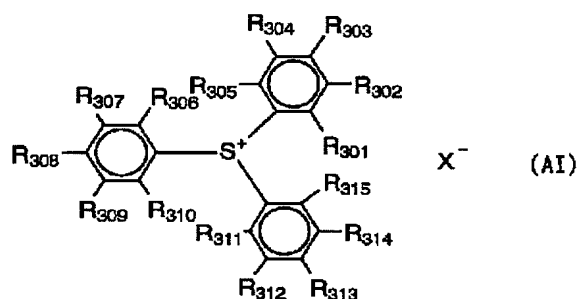
compound able to react using a periodate, and can compound the obtained iodonium salt by carrying out salt exchange to a corresponding carboxylic acid. The compound expressed with a general formula (II) and a general formula (III) makes the phenyl sulfoxide which is not permuted [aryl Grignard reagents, such as for example, aryl magnesium bromide, a permutation, or] react, and can compound the obtained triarylsulfonium halide by the approach of carrying out salt exchange with a corresponding carboxylic acid. Moreover, condensation, the approach of carrying out salt exchange, a diaryl iodonium salt, and a diaryl sulfide are [the phenyl sulfoxide which is not permuted / a permutation or / and a corresponding aromatic compound] compoundable by condensation, the approach of carrying out salt exchange, etc. using the catalyst of copper acetate etc. using acid catalysts, such as methansulfonic acid / diphosphorus pentaoxide, or an aluminum chloride. Once leading salt exchange to a halide salt, it can carry out salt exchange also of also using the approach of using silver reagents, such as silver oxide, and changing into carboxylate, or ion exchange resin. Moreover, the carboxylic acid or carboxylate used for salt exchange can be obtained by hydrolysis of commercial carboxylic-acid halide etc., using a commercial thing.

[0131] The thing using what is drawn from the fluoro aliphatic compound manufactured by the telomerization method (called the telomer method) or the co-oligomerization method (called the oligomer method) of the carboxylic acid by which the fluorine permutation was carried out as an anion part is also desirable. The manufacturing method of these fluoro aliphatic compounds is indicated by 117–118 pages of “composition of a fluorine compound, and a function” (editorial supervision: Nobuo Ishikawa, issuance:CMC Co., Ltd., 1987), and 747 – 752 pages of “Chemistry of Organic Fluorine Compounds II” (Monograph 187, Ed by Milos Hudlicky and Attila E. Pavlath, and American Chemical Society 1995), for example. The telomerization method is the approach of performing the radical polymerization of fluorine content vinyl compounds, such as tetrafluoroethylene, by making the large alkyl halide of chain transfer constants, such as an iodide, into TEROGEN, and compounding a telomer (the example was shown in Scheme-1). Although the mixture of two or more compounds with which chain length differs in composition by the telomer method is obtained, it may be used with mixture, and it may refine and this may be used.

[0132] [B-2b] As an ionicity compound which has fluorine a non-containing carboxylic acid as the compound which decomposes according to an operation of the ionicity compound acid which has fluorine a non-containing carboxylic acid as the compound which decomposes according to an operation of an acid and generates fluorine a non-containing carboxylic acid, and an anion, and generates fluorine a non-containing carboxylic acid, and an anion, the compound shown by the following general formula (A.I. Artificial Intelligence) – (AV) can be mentioned, for example.

[0133]

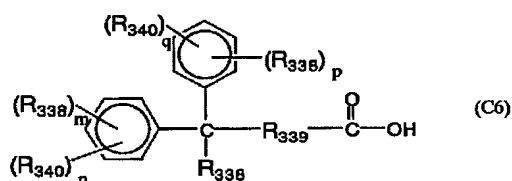
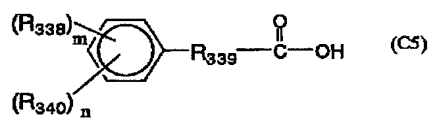
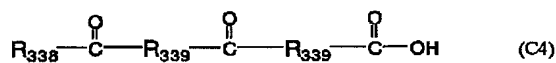
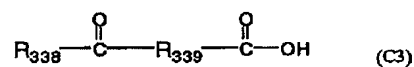
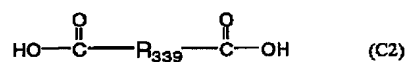
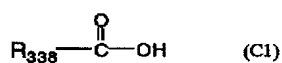
[Formula 51]



[0134] In the above-mentioned formula, R301 –R337 express a hydrogen atom, a straight chain, branching or an annular alkyl group, a straight chain, branching or an annular alkoxy group, a hydroxy group, a halogen atom, or zero –S–R independently respectively. R0 expresses a straight chain, branching, an annular alkyl group, or an aryl group. Ra and Rb express the alkyl group and alkoxy group which may have the hydrogen atom, the nitro group, the halogen atom, and the substituent independently respectively. Rc and Rd express the alkyl group or aryl group which may have the halogen atom and the substituent independently respectively. Rc and Rd may join together and the cyclic hydrocarbon (the oxygen atom and the nitrogen atom may be included in endocyclic [these]) of a ring, a monocycle, or many rings may be formed. Y1 and Y2 may express a carbon atom, and single bond or double association is sufficient as Y1–Y2 association. Above-mentioned X[–] expresses that from which the carboxylic-acid compound shown by the following formula became an anion. X1 and X2 express respectively that from which the carboxylic-acid compound shown by the following formula became an ester group in the carboxyl group part independently.

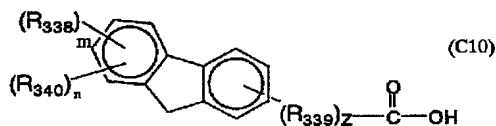
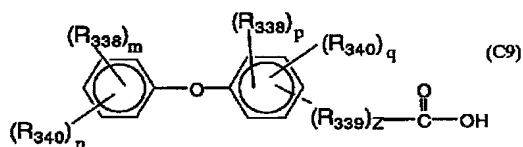
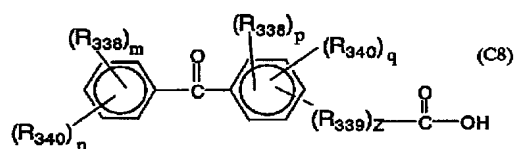
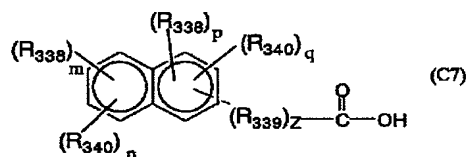
[0135]

[Formula 52]



[0136]

[Formula 53]



[0137] The inside of the above-mentioned formula and R338 are the shape of a straight chain, the letter of branching, or the annular alkyl group (it is here) of carbon numbers 1-30. Even if the oxygen atom and the

nitrogen atom are included in the chain of an alkyl group, the shape of a good straight chain of carbon numbers 1–20, The shape of the letter of branching or an annular alkenyl radical, and a straight chain of carbon numbers 1–20, the letter of branching, or an annular alkynyl group, The shape of a straight chain of carbon numbers 1–20, the letter of branching or an annular alkoxy group, the radical by which a part of hydrogen atom [at least] of said alkyl group was permuted with the halogen atom and/or the hydroxyl group, The permutation or the unsubstituted aryl group of the radical by which a part of hydrogen atom [at least] of said alkenyl radical was permuted with the halogen atom and/or the hydroxyl group, or carbon numbers 6–20 is shown. Here, as a substituent of an aryl group, an alkyl group, a nitro group, a hydroxyl group, an alkoxy group, an acyl group, an alkoxy carbonyl group, and a halogen atom can be mentioned.

[0138] R339 is the shape of single bond or a straight chain of carbon numbers 1–20, a letter of branching, or an annular alkylene group (it is here). Even if the oxygen atom and the nitrogen atom are included in the chain of an alkylene group, the shape of a good straight chain of carbon numbers 1–20, The letter of branching or an annular alkenylene group, the radical by which a part of hydrogen atom [at least] of said alkylene group was permuted with the halogen atom and/or the hydroxyl group, The radical by which a part of hydrogen atom [at least] of said alkenylene group was permuted by the halogen atom, or the ARUKOKI alkylene group of carbon numbers 2–20 is shown, R338 and R339 existing [two or more] may be the same to mutual, or they may differ in it.

[0139] R340 shows a hydroxyl group or a halogen atom, and R340 existing [two or more] may be the same to mutual, or may differ in it. Respectively, independently, m, n, p, and q are the integers of 0–3, and are $m+n \leq 5$ and $p+q \leq 5$. z is 0 or 1.

[0140] The thing of 1–4 carbon numbers like a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, and t-butyl in said general formula (A.I. Artificial Intelligence) – (AV) which may have a substituent as R301–R337, the straight chain in Ra, Rb, Rc, Rd, and R0, and a branching alkyl group is mentioned. As an annular alkyl group, the thing of 3–8 carbon numbers like a cyclo propyl group, a cyclopentyl group, and a cyclohexyl radical which may have a substituent is mentioned. As an alkoxy group of R301–R337, and Ra and Rb, the thing of 1–4 carbon numbers like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n-butoxy radical, an iso butoxy radical, a sec-butoxy radical, and a t-butoxy radical is mentioned. As R301–R337, and a halogen atom of Ra, Rb, Rc, and Rd, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. The thing of 6–14 carbon numbers which may have a phenyl group, a tolyl group, a methoxyphenyl radical, and a substituent like a naphthyl group as an aryl group of R0, Rc, and Rd is mentioned. The alkoxy group of 1–4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, iodine atom), the aryl group of 6–10 carbon numbers, the alkenyl radical of 2–6 carbon numbers, a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. are mentioned preferably as these substituents.

[0141] As a cyclic hydrocarbon (the oxygen atom and the nitrogen atom may be included in endocyclic [these]) of the ring and monocycle which Rc and Rd combine and form, or many rings, benzene structure, naphthalene structure, cyclohexane structure, norbornene structure, OKISA bicyclo structure, etc. are mentioned.

[0142] The sulfonium expressed with the general formula (A.I. Artificial Intelligence) used by this invention – (AIII) and an iodonium compound contain that from which the carboxyl group (–COOH) of at least one sort of

compounds became an anion ($-\text{COO}^-$) as the pair anion X^- among the carboxylic-acid compounds shown by above-mentioned formula (C1) – (C10). The compound expressed with general formula (AIV) used by this invention – (AV) contains the substituent from which the carboxyl group ($-\text{COOH}$) of at least one sort of compounds turned into an ester group ($-\text{COO}^-$) as substituents X1 and X2 among the carboxylic-acid compounds shown by above-mentioned formula (C1) – (C10).

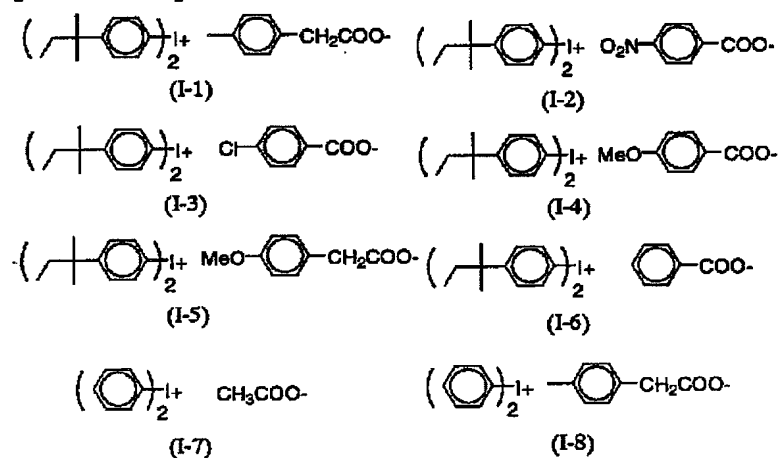
[0143] As the shape of a straight chain in R338 of carbon numbers 1–30, the letter of branching, or an annular alkyl group (here, the oxygen atom and the nitrogen atom may be included in the chain of an alkyl group), methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl, dodecyl, 1-ethoxyethyl, adamantyl, etc. are mentioned. Ethenyl, propenyl, isopropenyl, a cyclohexene, etc. are mentioned as the shape of a straight chain, the letter of branching, or the annular alkenyl radical of carbon numbers 1–20. Acetylene, pro PENIREN, etc. are mentioned as the shape of a straight chain, the letter of branching, or the annular alkynyl group of carbon numbers 1–20. As the shape of a straight chain, the letter of branching, or the annular alkoxy group of carbon numbers 1–20, methoxy and ethoxy ** propyloxy, butoxy one, cyclohexyloxy, iso butoxy, dodecyloxy, etc. are mentioned. Phenyl, naphthyl, anthranil, etc. are mentioned as the permutation or the unsubstituted aryl group of carbon numbers 6–20. As a substituent of an aryl group, an alkyl group, a nitro group, a hydroxyl group, an alkoxy group, an acyl group, an alkoxy carbonyl group, and a halogen atom can be mentioned.

[0144] If it considers as the shape of a straight chain in R339 of carbon numbers 1–20, the letter of branching, or an annular alkylene group (here, the oxygen atom and the nitrogen atom may be included in the chain of an alkylene group), methylene, ethylene, a propylene, a butylene, an isobutylene, ethoxyethylene, cyclo hexylene, etc. are mentioned. Vinylene, propine, etc. are mentioned as the shape of a straight chain, the letter of branching, or the annular alkenylene group of carbon numbers 1–20.

[0145] Although an example is shown, this invention is not limited to these.

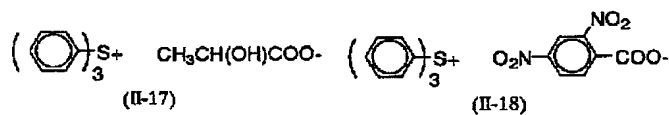
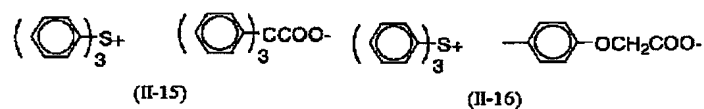
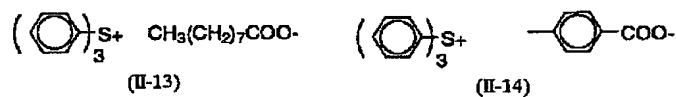
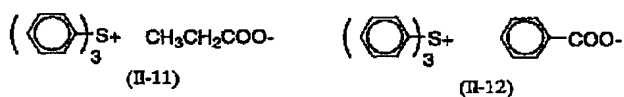
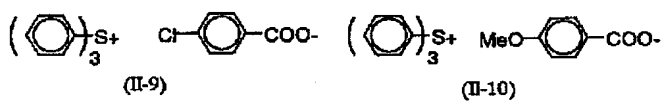
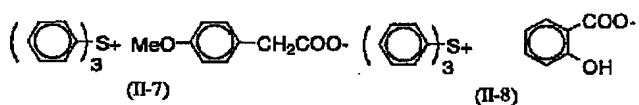
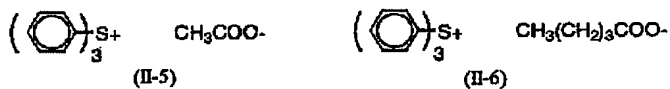
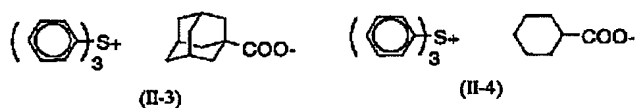
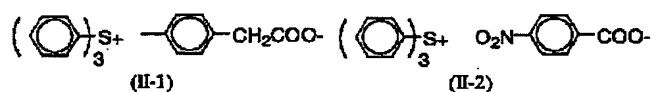
[0146]

[Formula 54]



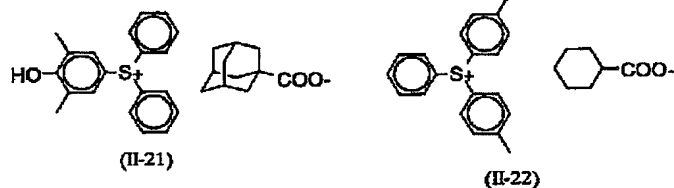
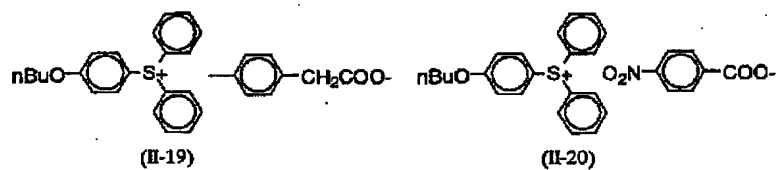
[0147]

[Formula 55]



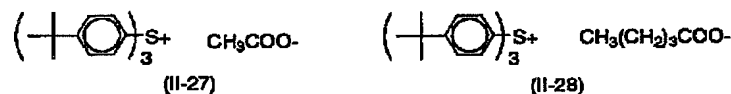
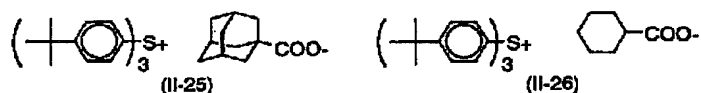
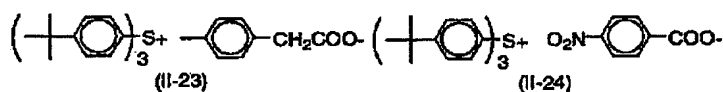
[0148]

[Formula 56]



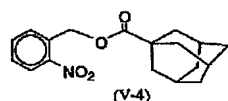
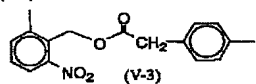
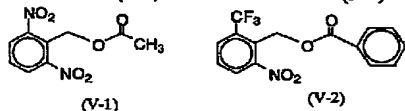
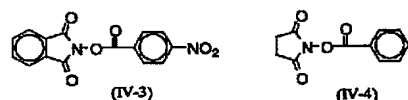
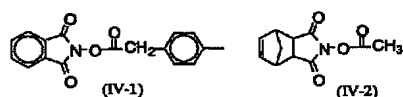
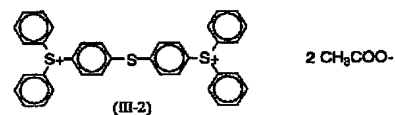
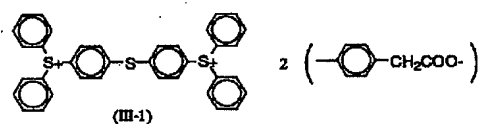
[0149]

[Formula 57]



[0150]

[Formula 58]



[0151] The compound expressed with a general formula (A.I. Artificial Intelligence), a general formula (AII), and a general formula (AIII) An approach given in a U.S. Pat. No. 3,734,928 description, Macromolecules, vol.10, 1307 (1977), Journal of Organic Chemistry, vol.55, 4222 (1990), J.Radiat.Curing, vol.5(1), and 2 (1978) It is compoundable by exchanging a counter anion further using the approach of a publication etc. The compound expressed with a general formula (AIV) and a general formula (AV) makes an N-hydroxy imide compound and carboxylic-acid chloride react on basic conditions, or is obtained by making nitrobenzyl alcohol and carboxylic-acid chloride react under a basic condition.

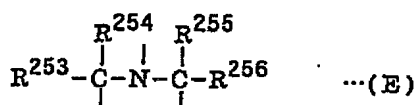
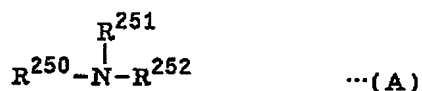
[0152] the above-mentioned B1a, the weight ratio of the addition of a B1b component, and the weight ratio of the addition of B1 component and B-2 component -- usually -- 1 / 1 - 100/0 -- desirable -- 1 / 1 - 10/1 -- it is 2 / 1 - 5/1 especially preferably. The total quantity of B1 component and B-2 component is 0.5 - 20 % of the weight usually 1 - 10% of the weight of the range more preferably 0.75 to 15% of the weight to

constituent total solids. Two or more B1 components and B-2 components may carry out seed content respectively.

[0153] [3] To the constituent of organic base nature compound this invention, after the exposure of an activity beam of light or a radiation, it is desirable to add an organic base nature compound in order to prevent the engine-performance fluctuation (T-top configuration formation of a pattern, sensibility fluctuation, pattern line breadth fluctuation, etc.) by the passage of time to heat-treatment, the engine-performance fluctuation by the passage of time after spreading, and superfluous diffusion (degradation of resolution) of the acid at the time of heat-treatment after the exposure of an activity beam of light or a radiation further. As an organic base nature compound, it is the organic base compound which contains basic nitrogen, for example, and four or more compounds are preferably used with the electric dissociation exponent value of a conjugate acid. Specifically, the structure of following type (A) – (E) can be mentioned.

[0154]

[Formula 59]



[0155] Here, it is R250 and R251. And R252 It may be the same, or you may differ and the permutation of a hydrogen atom, the alkyl group of 1–6 carbon numbers, the amino alkyl group of 1–6 carbon numbers, the hydroxyalkyl radical of 1–6 carbon numbers, or 6–20 carbon numbers or an unsubstituted aryl group is expressed, it may join together mutually and R251 and R252 may form a ring here. R253, R254, and R255 And R256 It may be the same, or you may differ and the alkyl group of 1–6 carbon numbers is expressed. Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [a permutation or] preferably.

[0156] As a desirable example, the aminopyridine which is not permuted [the guanidine which is not permuted / a permutation or / a permutation, or], The amino pyrrolidine which is not permuted [the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or], The pyrazole which is not permuted [the indazole which is not permuted / a permutation or /, an imidazole, a permutation, or], The

pyrimidine which is not permuted [the pyrazine which is not permuted / a permutation or /, a permutation, or], The amino alkyl morpholine which is not permuted [the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0157] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, [0158] 3-amino pyrrolidine, a piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, a 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, A pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, Although 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, etc. are mentioned, it is not limited to this. These nitrogen-containing basicity compounds are independent, or are used together two or more sorts.

[0159] As for the operating rate in the constituent of an acid generator and an organic base nature compound, it is desirable that it is a (acid generator) / (organic base nature compound) (mole ratio) = 2.5-300. This mole ratio may serve as low sensibility less than by 2.5, resolving power may decline, and if 300 is exceeded, **** of a resist pattern may become large by the passage of time to exposure afterbaking processing, and resolving power may also decline. a (acid generator) -- / (organic base nature compound) (mole ratio) -- desirable -- 5.0-200 -- it is 7.0-150 still more preferably.

[0160] [4] As for the constituent of surfactant this invention, it is desirable to contain a surfactant especially a fluorine system, and/or a silicon system surfactant. That is, it is desirable to contain either of the surfactants containing both a fluorochemical surfactant, a silicon system surfactant and a fluorine atom, and a silicon atom or two sorts or more in the constituent of this invention. Addition of these fluorines system and/or a silicon system surfactant has effectiveness in control of a development defect, and improvement in spreading nature.

[0161] As these surfactants, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, a U.S. Pat. No. 5405720 number, a U.S. Pat. No. 5360692 number, A U.S. Pat. No. 5529881 number, a U.S. Pat. No. 5296330 number, a U.S. Pat. No. 5436098 number, A U.S. Pat. No. 5576143 number, a U.S. Pat. No. 5296143 number, a U.S. Pat. No. 5294511 number, and a surfactant given in a U.S. Pat. No. 5824451 number can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of such marketing, for example, EFUTOPPU EF301, EF303, and EF352 (Made in formation [New Akita]), Fluorad 430 and FC 431

(Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink make), A fluorochemical surfactant or silicon system surfactants, such as the Asahi guard AG710, Sir chlorofluorocarbon S-382, SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (Troy chemical company make), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0162] The loadings of a surfactant are usually 0.01 % of the weight – 1 % of the weight preferably on the basis of the solid content in the constituent of this invention 0.001 % of the weight to 2% of the weight. You may add independently and these surfactants can also be added in some combination.

[0163] [5] Melt the constituent of solvent this invention to the solvent which dissolves the above (a) and the (b) component, and apply it on a base material. As a solvent used here, ethylene dichloride, a cyclohexanone, Cyclopentanone, 2-heptanone, gamma-butyrolactone, a methyl ethyl ketone, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, ethylene glycol monoethyl ether acetate, Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, Propylene-glycol-monomethyl-ether acetate, toluene, ethyl acetate, Methyl lactate, ethyl lactate, methoxy methyl propionate, ethoxy ethyl propionate, methyl pyruvate, pyruvic-acid ethyl, pyruvic-acid propyl, N.N-dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, a tetrahydrofuran, etc. are desirable, and independent in these solvents -- or it is mixed and used.

[0164] In manufacture of a precision integrated circuit device etc., on substrates (example: transparence substrates, such as silicon / diacid-ized silicon leather **, a glass substrate, and an ITO substrate etc.), the constituent of this invention can be applied, it can irradiate by the ability using an activity beam of light or radiation drawing equipment next, and the pattern formation process to a resist film top can form a good resist pattern heating, development, a rinse, and by drying.

[0165] As a developer of the constituent of this invention, a sodium hydroxide, a potassium hydroxide, Inorganic alkali, such as a sodium carbonate, a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as dimethylethanolamine and a TORIETA no amine, The water solution of alkali, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, and a choline, a pyrrole, and a piperidine, can be used. Furthermore, surfactants, such as alcohols, such as isopropyl alcohol, and the Nonion system, can also be used for the water solution of the above-mentioned alkali, carrying out suitable amount addition. the inside of these developers -- desirable -- quaternary ammonium salt -- they are tetramethylammonium hydroxide and a choline still more preferably.

[0166]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the content of this invention is not limited.

[0167] The example 1 (composition illustrated previously (F-1)) of <composition of A component> composition

3 - (2-hydroxy - [Then, 2-chloro methyl-2-hydroxy propane 21.6g was added to the place which melted 3 and 3-bis(trifluoromethyl) ethyl norbornene 54.8g to DMF, and NaOH8.0g was added in it.]) It heated at 100 degrees C then for 3 hours. After returning reaction mixture to a room temperature and adding 300ml of

ethyl acetate, after adding distilled water 1L, liquids were separated in the separating funnel, and the ethyl acetate layer was isolated preparatively. Again, added distilled water 1L, it was washed by performing liquid separation actuation in the separating funnel, and ethyl acetate layers were collected. 4-(norbornene methyl)- which refines with a silica gel column chromatography and becomes an alcoholic intermediate product after removing a solvent in an evaporator -- the 5, 5, and 5-trifluoro-2-methyl-4-trifluoromethyl pentanol was obtained. alpha-trifluoroacetic acid chloride and the above-mentioned alcohol were made to react under DBU existence, and the monomer was obtained. After adding 4-(2-hydroxy-hexafluoro isopropyl) styrene 13.5g and the above-mentioned monomer 23.4g to tetrahydrofuran (THF) 100ml, it heated to 65 degrees C under the nitrogen air current. Azo system polymerization initiator V-65 (product made from Wako Pure Chem Industry) 1.24g was added there, and it was made to react under 8-hour stirring as it is. After adding hexane 500ml to reaction mixture and settling a polymer, the upper layer was removed in the decantation. The ***** polymer which remained was melted to acetone 50ml, by adding hexane 1L again, judgment processing of the polymer was carried out and the unreacted monomer and the oligomer component were removed. When the determination of molecular weight was performed for the obtained polymer in GPC, weight average molecular weight was 14000 and degree of dispersion was 1.5. Resin (F-2) - (F-12) illustrated previously similarly was compounded. the mol of the resin (C1) of the obtained polymer and the example of a comparison -- a presentation ratio, weight average molecular weight, and degree of dispersion are shown in the following table 1.

[0168]

[A table 1]

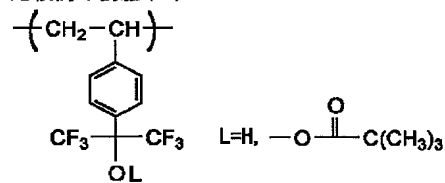
表1

樹脂	モノ組成比	重量平均 分子量	分散度
(F-1)	50/50	14000	1.5
(F-2)	50/50	12000	1.6
(F-3)	50/50	8500	1.8
(F-4)	50/50	6900	1.8
(F-5)	70/30	8500	1.6
(F-6)	70/30	16000	1.8
(F-7)	60/10/30	6900	1.8
(F-8)	60/10/30	7900	1.4
(F-9)	50/50	15000	1.4
(F-10)	60/40	9400	1.5
(F-11)	60/40	9800	1.6
(F-12)	50/50	9500	1.6
(C-1)	60/40	12000	1.9

[0169] The structure of the resin (C1) of the example of a comparison is shown below. In addition, resin (F-1) - (F-12) structure are [0170] illustrated previously.

[Formula 60]

比較例の樹脂 (C1)



L の t-Boc 化率 : 40%

[0171] Example 1 of <composition of B component> composition (composition of triphenylsulfonium NONAFURORO butane sulfonate (VII-4))

Triphenylsulfonium iodide 20g was dissolved in methanol 500ml, 12.5g of silver oxides was added to this, and it stirred at the room temperature for 4 hours. After filtering reaction mixture and removing a silver compound, NONAFUROROBUTAN sulfo nick acid 14.9g was added to this solution, and this solution was condensed. After adding diisopropyl ether 300ml to the obtained oily matter and fully stirring, the actuation except diisopropyl ether was repeated twice by decant. When reduced pressure drying of the obtained oily matter was carried out, 18g of specified substance was obtained.

[0172] Synthetic example 2 (composition of triphenylsulfonium-4-dodecylbenzene sulfonate (PAG 4-1))

Triphenylsulfonium iodide 10g was dissolved in methanol 500ml, 4.44g of silver oxides was added to this, and it stirred at the room temperature for 4 hours. After filtering reaction mixture and removing a silver compound, 4-dodecylbenzene sulfo nick acid 4.67g was added to this solution, and this solution was condensed. After adding diisopropyl ether 300ml to the obtained oily matter and fully stirring, the actuation except diisopropyl ether was repeated twice by decant. When reduced pressure drying of the obtained oily matter was carried out, 6g of specified substance was obtained.

[0173] Synthetic example 3 (composition of triphenylsulfonium nona FURORO pentanoate (II-4f))

Triphenylsulfonium iodide 20g was dissolved in methanol 500ml, 12.5g of silver oxides was added to this, and four intervals of clear weather were agitated at the room temperature. After filtering reaction mixture and removing a silver compound, nona FURORO pentanoic acid 14.9g was added to this solution, and this solution was condensed. After adding diisopropyl ether 300ml to the obtained oily matter and fully agitating, the actuation except G SOPUROIPIRUETERU was repeated twice by decant. When reduced pressure drying of the obtained oily matter was carried out, 18g of specified substance was obtained.

[0174] 1.2g of resin shown in examples 1-12 and the [example [of a comparison] 1] following table 2, acid-generator B1 component:0.024g, acid-generator B-2 component:0.006g, a surfactant: The polymer solution which dissolved 100 ppm and organic base nature compound:0.0012g in 19.6g of solvents to the polymer solution was filtered with the 0.1-micrometer Teflon (trademark) filter, and positive-resist liquid was prepared.

[0175]

[A table 2]

表2

実施例	樹脂	酸発生剤(D1) (重量比)	酸発生剤(D2)	溶剤 (重量比)	有機塩基性 化合物	界面 活性剤
1	(F-1)	(VII-4)		S-2	N-1	H-1
2	(F-2)	(VII-14)		S-2	N-1	H-1
3	(F-3)	(VII-4)		S-2	N-2	H-1
4	(F-4)	(VII-24)		S-2	N-1	H-1
5	(F-5)	(VII-4)		S-2	N-1	H-1
6	(F-6)	(VII-14)		S-2	N-1	H-2
7	(F-7)	(VII-36)/(PAG4-1) 50/50		S-2/S-3 90/10	N-1	H-1
8	(F-8)	(VII-44)/(PAG4-1) 50/50		S-2	N-1	H-1
9	(F-9)	(VII-54)	(II-4f)	S-2	N-1	H-1
10	(F-10)	(VII-36)/(PAG4-1) 50/50	(II-5f)	S-2	N-1	H-1
11	(F-11)	(VII-4)		S-2	N-2	H-2
12	(F-12)	(VII-4)		S-2	N-1	H-1
比較例 1	(C-1)	(VII-4)		S-2	N-1	H-1

[0176] The content of the notation in a table 2 is as follows.

N-1: A hexamethylenetetramine N-2:1, 5-diazabicyclo [4.3.0]-5-nonene W-1 : megger fuck F176 (Dainippon Ink & Chemicals, Inc. make) (fluorine system)

W-2: Megger fuck R08 (Dainippon Ink & Chemicals, Inc. make) (a fluorine and silicon system)

S-2: Propylene-glycol-monomethyl-ether acetate S-3 : propylene glycol monomethyl ether [0177] The positive-resist liquid prepared as mentioned above was applied to homogeneity on the silicon wafer which applied the antireflection film (DUV42-6 BrewerScience.Inc. make) using the spin coater, stoving was performed for 120-degree-C 60 seconds, and the positive-resist film of 0.1 micrometers of thickness was formed. Pattern exposure was carried out using the mask for a line and tooth spaces (line breadth: 160nm, a line / tooth-space =1/1) using the micro stepper, and it heated on the hot plate for 110-degree-C 90 seconds immediately after exposure to this resist film. Negatives were developed for 30 seconds at 23 degrees C with the tetramethylammonium hydronalium oxide water solution 2.38 more%, and it dried, after carrying out a rinse with purity for 30 seconds. Thus, the following approach estimated the resist engine performance for the pattern on the obtained silicon wafer.

[0178] [Line edge roughness] About the range of edge 5micrometer of the longitudinal direction of a line pattern, the distance from the datum line which should have an edge was measured 50 point by length measurement SEM (Hitachi Make S-8840), it asked for standard deviation, and 3sigma was computed. It is shown that a value is small that it is such good engine performance.

[0179] [Development defect] About the resist pattern obtained as mentioned above, the number of development defects was measured by the KLA-2112 set by the KEERUE ten call company, and the acquired primary data value was made into the measurement result. A performance-evaluation result is shown in the following table 3.

[A table 3]

表3

実施例	ラインエッジラフネス(nm)	現像欠陥数(個)
1	9.9	15
2	11.2	16
3	13.5	18
4	10.9	16
5	11.8	18
6	12.4	21
7	8.6	26
8	8.8	19
9	8.9	25
10	8.6	25
11	10.0	19
12	12.5	18
比較例1	15.6	73

[0180] The result of a table 3 shows that line edge roughness and a development defect are small, and the constituent of this invention is good.

[0181]

[Effect of the Invention] By this invention, the positive-resist constituent with which line edge roughness and a development defect have been improved can be offered.

[Translation done.]